Investigation of CO₂ Capture Systems, Lewis Acid-Base Pairs, and
Oscillating Reactions with Electronic Structure Theory and Kinetics-Based Approaches

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by

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Oscillating Reactions with Electronic Structure Theory and Kinetics-Based Approaches

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ABSTRACT

Equilibrium is a key theme in chemistry education. Starting in high school and continuing in freshman general chemistry courses, STEM students have to learn the foundations of equilibria. What is the key concept of an equilibrium? How can we describe an equilibrium? The concept of an equilibrium constant K is introduced, and its relation to the Gibbs enthalpy ΔG^0 is noted. The equilibrium constant K also is related in a straightforward manner to the forward and backward reaction rate constants. Usually, a few simple applications are discussed, primarily in the area of acid-base chemistry. The topic is revisited in organic chemistry and clarified conceptually with reaction energy diagrams.

To study equilibrium as a student is one thing, and to study equilibrium problems as a researcher is quite another. How does one determine equilibrium constants and how does one determine reaction rate constants? What do we know about the accuracy of the experimental quantities reported in the literature? How does one deal with multi-equilibria? How does one account for non-ideal conditions and concentrated solutions? Over the last six years, I have learned how to approach and solve all of these issues. One of the most stunning insights was the realization that

even so-called non-linear reactions can in fact be described in some cases by application of complicated systems of equilibrium reactions.

The Glaser group very strongly believes that the interplay between experimental and theoretical work is vitally important to really understand a problem. This combination builds a strong focus on quantitative aspects and it often also leads to new insights that might not be attainable from experimentation or modeling alone. The five chapters presented here show that this two-pronged approach is widely applicable to several areas of chemistry. The two main topics of our studies have been carbon dioxide capture from air and reaction mechanisms of oscillating chemical systems. All of the chapters in my dissertation do have a very strong connection between theory and experimentation. I studied both aspects in most cases. Only in one case (Chapter 5) did I not perform the experiments, but even in this case, a very deep engagement with the experimental literature was required to solve a decades-long discrepancy.

Chapter 1 is about the study of equilibria between different conformations of substrates and products and an evaluation of their effects on the overall reaction energy. Specifically, we studied the capture of CO₂ by small alkylamines. The quality of that discussion was tested directly with the work described in Chapter 2. The work that led to Chapter 2 was an enormous learning experience; it was amazing to see all the pieces of the complicated multi-equilibrium system come together to determine the ΔG^0 of the carbamylation of butylamine in aqueous solution.

The interest in equilibria actually began with the quest of the non-linear dynamics group to understand oscillating chemical reactions. From the outset, this quest was pursued as an interdisciplinary project between chemistry and mathematics. My work with the dynamics group resulted in Chapters 3 and 4 of the present dissertation. Chapter 3 is a re-evaluation of the video-

based kinetic analysis with high temporal resolution and over long timescales. The colorimetric studies revealed unexpected “hysteresis loops” in cerium-catalyzed Belousov-Zhabotinsky oscillating reactions. We studied the reaction progress in RGB space because we wanted to learn under what conditions the video-based analysis would allow for quantitative concentration determinations. The desire to assess the quality of the video-based analysis in RGB space, led to the serendipitous discovery of hysteresis loops. The origins of Chapter 4 had to do with the question as to whether accounting for ionic strength would be essential to obtain accurate simulations of BZ reactions. The goal of my work on phosphate buffers was an evaluation of the usefulness of Debye-Hückel theory to electrolyte solutions with highly-charged ions present in significant concentrations. The phosphate buffer systems are widely in use and outstanding experimental sets of pH values were available to really test the performance of the solution models.

Many years of studies of the Lewis acid-base pair $\text{F}_3\text{B} \leftarrow \text{PH}_3$ illustrate in a beautiful fashion what can go wrong when experimentalists interpret their data based on inaccurate theory and when computational chemists do not seek consistency with existing experimental data published in the literature. A careful read of the literature clearly showed early on that experimental and theoretical reports on $\text{F}_3\text{B} \leftarrow \text{PH}_3$ are entirely inconsistent. It took years to explain what was actually measured, namely the compound $\text{F}_2\text{B}-\text{PH}_2$, and to explain why many theoretical reports predicted the wrong dative-bonding geometry.

Chapter 1 Computational Investigation of the Thermochemistry of the CO₂ Capture Reaction by Ethylamine, Propylamine, and Butylamine in Aqueous Solution Considering the Full Conformational Space *via* Boltzmann Statistics.

1.1. Introduction

As of May 2019, the global concentration of CO₂ in the atmosphere has reached 411.04 ppm,¹ and there has been no slowing of the rate of atmospheric CO₂ increase (*ca.* 15 ppm/decade). Drastic cutbacks of CO₂ emissions and more complete CO₂ capture at concentrated sources and current negative emissions technologies²⁻⁵ will not be sufficient to reverse trends. Even at current atmospheric CO₂ levels, it will not be possible to halt global climate change because natural CO₂ capture is a slow process.^{6,7} Thus there is a clear need for the development of new methodologies for CO₂ capture of carbon dioxide from ambient air.^{8,9} Amine based CO₂ capture has been widely studied and aqueous amines are by far the most common systems used for capturing CO₂ at concentrated sources.

Scheme 1-1. From Rubisco to the Tetrapeptide KDDE

The energy required to release CO₂ after its capture is the limiting factor for large-scale CO₂ extraction from air using capture-and-release systems. We have been interested in developing rubisco-based biomimetic systems for reversible CO₂ capture from ambient air.¹⁰⁻¹² Ribulose-1,5-bisphosphate carboxylase/oxygenase (rubisco) is the enzyme responsible for most of the carbon fixation of the CO₂ from air.¹³ The active site of spinach rubisco (1AUS, Scheme 1-1) contains the amine group of the side chain of Lys(201) and a hydrated magnesium ion that is held in place by the carboxylic acid groups of Asp(203) and Glu(204).¹⁴ In order to accomplish its enzymatic activity, the amine group of the active site lysine must be carbamylated.^{15,16} We suggested that this carbamylation reaction is a suitable capture-and-release system (CRS) and that the Mg²⁺-complexed tetrapeptide KDDE (Scheme 1-1) presents the smallest chemical implementation. Computational studies of KDDE models suggest that this CRS features the desired thermodynamic characteristics.^{10,11} A good candidate for reversible CO₂ capture meets two criteria: The spontaneity of the capture reaction at a given temperature; and the spontaneity of the reverse reaction under different temperature conditions. In other words, the spontaneity of the reaction should be primarily controlled by the entropic components. An ideal capture reaction will be both highly exergonic for efficient loading and highly ex-entropic for efficient removal of CO₂. We have been measuring the thermodynamics of the CO₂ capture by the KDDE tetrapeptide in the presence and absence of Mg²⁺ ions and as a function of pH. To discern the importance of the Mg²⁺ complexation, it became necessary to study CO₂ capture by the lysine side chain itself.

Scheme 1-2. Alkylamine and Alkylcarbamic Acid (R = Et, Pr, Bu)

Here, we report the results of computational studies of the thermodynamics of CO₂ capture by small alkylamines in aqueous solution. Specifically, we studied CO₂ addition to ethylamine Et-**1**, propylamine Pr-**1**, and butylamine Bu-**1** at room temperature with consideration of the full conformational space for the amine R-**1** and the corresponding carbamic acids R-**2** and R-**3** (Scheme 1-2). R-**2** and R-**3** are the *trans* and *cis* amides, respectively. The common procedure for the calculation of reaction energies involves the energies of the most stable structure (MSS) of each species involved in the reaction, and we will show those results. In addition and to achieve more accurate results, we also determined the reaction thermodynamics based on the Boltzmann average of the Gibbs free energy over all of the conformers. This undertaking presents significant challenges and these include (a) the consideration of all possible conformations, (b) the possible degeneracy of chiral structures, and (c) the determination as to whether a stationary structure contributes significantly to the Boltzmann analysis. Scheme 1-3 shows all possible non-eclipsed structures for a RCH₂-N(sp²)HX system. If the R group is achiral, then R-A and R-A', R-B and R-B', and R-C and R-C' are enantiomers. Table 1-1 aids in the enumeration of the stationary structures, and it shows for example that 48 out of 54 possible local minima need to be considered for butylcarbamic acid. We will show that a correct understanding of the RCH₂-NHCO₂H rotational profile affects the Boltzmann analysis.

Scheme 1-3. Non-eclipsed Structures of C–N Conformers of a $\text{RCH}_2\text{--N}(\text{sp}^2)\text{HX}$ System

Table 1-1. Enumeration of Unique Trial Structures and Minima

Molecule and Type	Number of unique trial structures	Number of unique, asym. local minima located	Number of unique, sym. local minima located	Number of local minima used in Boltzmann Analysis N_{total}
Et-1	2	1	1	3
Et-2	3	2 ^a	0	2
Et-3	3	2 ^a	0	2
Pr-1	5	4	1	9
Pr-2	9	4	0	8
Pr-3	9	4	1 ^a	8
Bu-1	14	13	1	27
Bu-2	27	11	1 ^a	22
Bu-3	27	13	1 ^a	26

^aIncludes a local minimum on PES, but not counted in population analysis, see text.

1.2. Computational Methods

Structure optimizations and analytical frequency calculations were performed using

Gaussian16¹⁷ using the APFD density functional¹⁸ and the polarized triply-split valence basis set

6-311G*.¹⁹⁻²¹ Implicit water solvation was incorporated *via* the Solvation Model Based on Solute Electron Density (SMD).²²

For each unique amine structure, we report in Table 1-2 the total energy (E , in a.u.), vibrational zero-point energy (VZPE, in kcal/mol), thermal energy (TE , in kcal/mol), and molecular entropy (S , in cal mol⁻¹ K⁻¹). In the Appendix, Table 1-5 reports the same information for the all carbamic acids conformers for the ethyl, propyl, and butyl systems.

Table 1-2. Thermodynamic Properties and Relative Energies^a for all Amine Conformers

Species	Energy	VZPE	TE	<i>S</i>	ΔE_{rel}	ΔG_{rel}	<i>P_i</i>
CO ₂	-188.486130	7.31	8.96	51.08		0.00	100.0
Ethylamine							
Et-1t	-135.090187	58.51	61.32	65.41	0.00	0.00	73.9
Et-1g (2)	-135.088981	58.64	61.36	64.65	0.76	1.03	13.1
Propylamine							
Pr-1tg (2)	-174.379037	76.65	80.10	71.89	-0.09	0.07	23.7
Pr-1tt	-174.378888	76.55	80.08	72.37	0.00	0.00	26.7
Pr-1gg (2)	-174.377422	76.73	80.16	71.77	0.92	1.18	3.6
Pr-1gt (2)	-174.377635	76.63	80.13	72.22	0.79	0.89	6.0
Pr-1gq (2)	-174.376938	76.57	80.07	72.35	1.22	1.23	3.4
Butylamine							
Bu-1tgg (2)	-213.667383	94.75	98.93	78.86	0.12	0.41	7.7
Bu-1tgt (2)	-213.667580	94.57	98.83	79.51	0.00	0.00	15.5
Bu-1tgq (2)	-213.664572	94.88	99.02	78.36	1.89	2.42	0.3
Bu-1ttg (2)	-213.666499	94.63	98.91	79.79	0.68	0.67	5.0
Bu-1ttt	-213.667383	94.53	98.87	79.97	0.12	0.02	15.0
Bu-1ggg (2)	-213.665782	94.85	98.99	78.37	1.13	1.63	1.0
Bu-1ggt (2)	-213.666025	94.65	98.90	79.26	0.98	1.11	2.4
Bu-1ggq (2)	-213.663194	94.70	98.90	78.97	2.75	2.98	0.1
Bu-1gtg (2)	-213.665511	94.66	98.91	79.44	1.30	1.40	1.5
Bu-1gtt (2)	-213.666171	94.55	98.87	79.81	0.88	0.83	3.8
Bu-1gtq (2)	-213.665135	94.58	98.89	80.19	1.53	1.39	1.5
Bu-1gqg (2)	-213.662641	94.61	98.85	79.65	3.10	3.08	0.1
Bu-1gqt (2)	-213.665543	94.45	98.77	80.12	1.28	1.03	2.7
Bu-1gqq (2)	-213.665219	94.68	98.89	79.25	1.48	1.62	1.0

a) *E* given in Hartrees, *TE* given in kcal/mol, *S* given in cal mol⁻¹ K⁻¹, ΔG_{rel} given in kcal/mol and *P_i* is the percentage of molecules that exist as that conformer according to the Boltzmann statistics. A (2) behind the conformer descriptor indicates that the structure has an enantiomer that is included in the Boltzmann analysis.

For molecules which can adopt several stereoisomeric structures, we also report the relative stabilities ΔG_{rel} (in kcal/mol) relative to the most stable stereoisomer. Based on the calculated relative energies ΔG_{rel} , we determined their individual contributions at temperature *T* = 298.15 K using the Boltzmann distribution (Eq. 1).

$$f_i = \frac{N_i}{N_{\text{total}}} = \frac{e^{-G_i/RT}}{\sum_{j=1}^{N_{\text{total}}} e^{-G_j/RT}} \quad (\text{Eq. 1})$$

The evaluation of equation 1 requires the knowledge of the stabilities G_j of all possible stereoisomers (N_{total}) and the population fraction $f_i = N_i/N_{\text{total}}$ for a given stereoisomer i . The population of each stereoisomer in percent, $P_i = N_i/N_{\text{total}} \times 100\%$, is reported in the last column of Table 1-2 for the amines and Table 1-5 (Appendix) for the carbamic acids.

For the capture reaction $\mathbf{AM} + \text{CO}_2 \rightarrow \mathbf{CA}$, the reaction free energy ΔG is determined as the difference between the sums of the energies of products and starting materials. The fastest approximation is based on the evaluation of the reaction energy using the most stable structure of each species, S , and we will call this $\Delta G_{\text{MSS}}(S)$. A better approximation to the reaction free energy considers the average energy of each species based on the populations and stabilities of its isomers, $\Delta G_{\text{BD}}(S)$. Equation 2 is used to determine the free energy of any given molecule as a sum of the energies of each conformer. However, these free energies are more intuitive when reported relative to the most stable structure, and equation 2 can be adapted to give equation 3.

$$\langle G \rangle = \sum_{i=1}^{N_{\text{total}}} f_i G_i \quad (\text{Eq. 2})$$

$$\langle G_{\text{rel}} \rangle = \sum_{i=1}^{N_{\text{total}}} f_i G_{\text{rel},i} \quad (\text{Eq. 3})$$

The calculation of the free energies of reaction are then given by equations 4-6. Equation 4 is the traditional approach, using only the free energies of the most stable structures of the products and reagents. Equation 6 accounts for the contribution to the reaction free energy from the other conformers.

$$\Delta G_{\text{MSS}} = G(\mathbf{CA}_{\text{MSS}}) - G(\mathbf{AM}_{\text{MSS}}) - G(\text{CO}_2) \quad (\text{Eq. 4})$$

$$\Delta G_{\text{BD}} = \langle G(\mathbf{CA}) \rangle - \langle G(\mathbf{AM}) \rangle - G(\text{CO}_2) \quad (\text{Eq. 5})$$

$$\Delta G_{\text{BD}} = \Delta G_{\text{MSS}} + \langle G_{\text{rel}}(\mathbf{CA}) \rangle - \langle G_{\text{rel}}(\mathbf{AM}) \rangle \quad (\text{Eq. 6})$$

The same equations apply to the Helmholtz free energy, ΔA , of the reactions. By definition, $\Delta G = \Delta A + \Delta(pV)$. The pV term is important in gas-phase thermochemistry. However, in condensed phase, $pV \approx 0$ because the expansion of the solution is almost negligible relative to the expansion of gases. Therefore, the ΔA value may be a better estimate of the spontaneity of reaction in condensed phase, and ΔA is 0.592 kcal/mol less than ΔG .

1.3. Results and Discussion

1.3.1. Enumeration of Conformations of Ethylamine and N-Ethylcarbamic Acid

1.3.1.1. Possible Structures

Newman projections along the N–C1 bond of the expected conformations of ethylamine and of ethylcarbamic acid are shown in Scheme 1-4. Throughout, we chose to orient the C1–C2 bond as shown in Scheme 1-4. Molecular models of the optimized structures of ethylamine and of ethylcarbamic acid are shown in Figure 1-1-1.

The conformers of ethylamine **Et-1t** and **Et-1g** differ in the orientation of the N-lone pair. Each conformation can be described by one of two dihedral angles $\eta_a = \angle(\text{H}_a\text{--N--C1--C2})$ and $\eta_b = \angle(\text{H}_b\text{--N--C1--C2})$. To facilitate the discussion, we will simply refer to these two conformations as **t** and **g** depending as to whether the N-lone pair is *trans* or *gauche* with respect to the C1–C2 bond (τ_1). There are of course two *gauche* conformations **g** and **g'** (the enantiomer of **g**) and both of these will matter in the Boltzmann statistical analysis (*vide infra*). Here we do show both **Et-1g** and **Et-1g'**, but in the structural discussions below we will consider only one unique structure of any pair of enantiomers, and these will usually be analogs of **Et-1g**.

Scheme 1-4. Conformations of Ethylamine and Ethylcarbamic Acid

The conformers of ethylcarbamic acid **Et-2t**, **Et-2c**, and **Et-2h** differ in the position of the COOH group. Formally **Et-2t** results by replacement of H_b in **Et-1t** by the COOH group. Of course, one could also replace H_a with COOH and generate the enantiomer **Et-2t'** which is not shown for brevity. Structures **Et-2c** and **Et-2h** result by replacement of H_b or H_a in **Et-1g**, respectively, and the names reflect whether the N–COOH bond or the remaining N–H bond is in a *trans* position relative to the C1–C2 bond. As always, **Et-2c'** and **Et-2h'** refer to the enantiomeric structures. The carbamic acids usually are trigonal planar about the N atom, and the Newman projections shown in the bottom row of Scheme 1-4 are more appropriate. For

structures of type **Et-2t**, the N-planarization does not cause any eclipsing, while structures of types **Et-2c** and **Et-2h** inadvertently would contain one near-eclipsed conformation. In other words, such structures will have a driving force to at least some degree of N pyramidalization to avoid such eclipsing as much as possible. For this reason, the schematic Newman projections shown in the second row are advantageous for the enumeration of complete conformational space and they will be used in the subsequent discussions of the larger alkylcarbamic acid structures.

As shown in Scheme 1-2, the carbamylation reaction can form two geometric isomers of carbamic acid. The *trans* amide **2** is generally preferred over the *cis* isomer **3**. Both species were investigated in every case. The equilibration between **2** and **3** does not require rotation about the N–CO₂H bond but can be accomplished very fast by proton transfer. Therefore, the Boltzmann statistical population analysis was performed on the set of all carbamic acid structures rather than on the subsets of structures **2** and **3**.

Figure 1-1. Optimized structures of unique conformers of ethylamine. Newman projections are shown with respect to the N-C1 bond. The number in parentheses is the population percentage in the Boltzmann analysis at 298 K for a single unique enantiomer.

1.3.1.2. Models of Local Minima

Molecular models of all of the optimized structures of ethylamine and ethylcarbamic acid are shown in Figure 1-1. Here and elsewhere, we show the schematic Newman projection of

conformations that were considered as initial trial structures but did not correspond to a stationary structure on the respective potential energy surface. For **2** and **3**, we were able to locate two conformers while all attempts to locate **Et-2h** or **Et-3h** led to one of the existing stationary structures. In Table 1-5 (Appendix), we include one row for every expected carbamic acid structure and explicitly indicate if such an expected structure does not exist.

The energies and relative stabilities of ethylamine are listed in Table 1-2. **Et-1t** is a C_s -symmetric structure and it is unique. On the other hand, **Et-1g** is an asymmetric structure and so there also exists its enantiomer **Et-1g'**. Table 1-1 contains one row for such a set of enantiomers and the number of symmetry-related stationary structures is indicated in parentheses following the structure descriptor.

The preferred conformation of ethylamine in the gas phase was determined by microwave spectroscopy²³ and it is **Et-1t** and the same is true in aqueous solution. The preferred conformation of ethylcarbamic acid is **Et-2t**, that is, the *trans* amide geometry is greatly preferred in the carbamic acid context compared the respective *cis* amide **Et-3t**. We also find a *trans* amide preference for the pair **Et-2c** and **Et-3c**.

1.3.1.3. Potential Energy Surface for EtNH–COOH Torsion

There is the possibility for C_s -symmetry for **Et-2c** and **Et-3c**. A scan of the dihedral angle $\chi = \angle(\text{HO}_2\text{C}-\text{N}-\text{C1}-\text{C2})$ in both **Et-2** and **Et-3** is shown in Figure 1-2 and we first discuss the situation for **Et-3**.

Figure 1-2. PES scans of the dihedral angle $\chi = \angle(\text{HO}_2\text{C}-\text{N}-\text{C1}-\text{C2})$ for the ethylcarbamic acids **Et-2** and **Et-3**. Plots on the left show the full χ range and plots on the right are close ups of the regions containing **Et-2c** and **Et-3c**. Relative E in kcal/mol.

The C_s-symmetric structure **Et-3c** is a local minimum on the PES but a very shallow one ($\nu_1 = 29 \text{ cm}^{-1}$). A scan in the vicinity of **Et-3c** as a function of the dihedral χ shows that the barrier to rotation about the N–C1 bond is merely $\Delta E = 0.470 \text{ kcal/mol}$ and lower than the thermal energy associated with the ν_1 mode of C_s-**Et-3c** (0.593 kcal/mol). Thus, C_s-**Et-3c** does *not* correspond to local minimum, instead it is an *unbound minimum* (UBM) and not considered in the Boltzmann analysis. Essentially, the entire **Et-3c** region is a transition state region for the enantiomerization **Et-3t** $\rightleftharpoons$ **Et-3t'**. The situation for **Et-2** is qualitatively similar except that the sink for **Et-2c** is even more shallow than **Et-3c**. The top-right panel of Figure 1-2 shows that the **Et-2c** region is very flat and contains a C_s-symmetric transition state structure ($\nu_1 = 115 \text{ cm}^{-1}$) between a pair of C₁ minima. Structures of the type **Et-2c** are UBMs and, essentially, the entire **Et-2c** region is a transition state region for the enantiomerization **Et-2t** $\rightleftharpoons$ **Et-2t'**.

The sinks around **Et-3t** and its enantiomer are shallow, containing at most two bound vibrational states for the normal mode promoting the rotation about the C1–N bond ($\nu_2 = 108\text{ cm}^{-1}$). The sinks around **Et-2t** and **Et-2t'** are even more shallow and contain only one bound vibrational state for the normal mode promoting the rotation about the C1–N bond ($\nu_2 = 108\text{ cm}^{-1}$). Therefore, **Et-3** is a fluxional molecule with equal populations of **Et-3t** and **Et-3t'**, and **Et-2** is a highly fluxional molecule with equal populations of **Et-2t** and **Et-2t'**.

1.3.1.4. Relative Energies and Population Analysis

The number of species entering the Boltzmann statistical analysis is listed in Table 1-1. For the ethylamine species, there were only three structures: **Et-1t**, **Et-1g** and **Et-1g'**. At room temperature, **Et-1t** was more favorable than the gauche conformers by 1.03 kcal/mol, and therefore 73.9% of the molecules exist in this conformation at any given time. Thus, 26.1% of the ethylamine molecules will exist in either one of the two gauche conformations. The ethylcarbamic acids were treated as a single set in the Boltzmann analysis. Because the **Et-Xh** conformers could not be located as local minima, they are not included in the statistical analysis. The transition state **Et-2c** and the unbound minimum **Et-3c** are also not included in the statistical analysis. Therefore, only the asymmetric **Et-2t** and **Et-3t** and their enantiomers are included in the Boltzmann analysis, for a total of four species. The *trans* amides are more favorable than the *cis* analogs by 1.22 kcal/mol and they have significantly more contribution to the overall population at room temperature. **Et-2t** and **Et-2t'** combined account for 88.7% of the overall population of ethylcarbamic acid at room temperature and the remaining 11.3% is split between the two *cis* conformers.

Table 1-3 lists the Gibbs free energies of the most stable structures (MSS) of the ethylamine and ethylcarbamic acid, and identifies those structures as **Et-1t** and **Et-2t**. It also lists the average Gibbs free energy, $\langle G_{298} \rangle$, for those species calculated using all of the conformers and their population fractions, based on equations 1 and 2. The difference between the averaged free energy and the free energy of the most stable structure, $\langle G_{\text{rel}} \rangle$, is given in the final column in kcal/mol. Based on these values and the free energy of CO₂, the reaction energies were calculated for the CO₂ capture reaction by ethylamine and appear at the bottom of Table 1-3. In the case of the most stable structures, the capture reaction free energy would be the ΔG for reaction R1.

When using the Boltzmann averaged energy values, the ΔG_{BD} reflects the energy difference between the average molecular energy of an ethylcarbamic acid molecule and the energy of the average ethylamine molecule. The Helmholtz free energies for the capture process are also provided in Table 1-3 for the reasons discussed above.

Table 1-3. Calculated Thermodynamic Values for the Capture Reaction

Molecule/Reaction	G_{298} of MSS		$\langle G_{298} \rangle$	$\langle G_{\text{rel}} \rangle$
CO ₂	-188.495174			
Ethylamine	-135.022601	Et-1t	-135.022175	0.27
Ethylcarbamic Acid	-323.521874	Et-2t	-323.521655	0.14
Propylamine	-174.284721	Pr-1tt	-174.284232	0.31
Propylcarbamic Acid	-362.784720	Pr-2tg	-362.784248	0.30
Butylamine	-213.546914	Bu-1tgt	-213.546154	0.48
Butylcarbamic Acid	-402.046920	Bu-2ttt	-402.046143	0.49
		ΔA_{BD}	ΔG_{MSS}	ΔG_{BD}
R1: Et-1t + CO ₂ → Et-2t		-1.98	-2.57	-2.70
R2: Pr-1tt + CO ₂ → Pr-2tg		-2.43	-3.03	-3.04
R3: Bu-1tgt + CO ₂ → Bu-2ttt		-2.50	-3.03	-3.02

G_{298} and $\langle G_{298} \rangle$ in Hartree, $\langle G_{\text{rel}} \rangle$ and reaction energies in kcal/mol.

1.3.2. Enumeration Conformations of Propylamine and N-Propylcarbamic Acid

1.3.2.1. Possible Structures

Newman projections of the conformations of propylamine and of propylcarbamic acid are enumerated using Schemes 1-5 and 1-6.

Scheme 1-5. Investigated Conformations of Propylamine

Scheme 1-6. Potential Conformations of Propylcarbamic Acid

As with ethylamine, the first letter describes the conformation about the N–C1 bond. The extension of the carbon skeleton requires one more label to describe the conformation about the C1–C2 bond, i.e., the dihedral angle $\tau_2 = \angle(\text{N}-\text{C1}-\text{C2}-\text{C3})$. There are at most three possibilities for the relative orientation between the terminal CH₃ group and the amino group. The Newman projections on the top row are derivatives of **Et-1t** and in **Pr-1tt** the terminal methyl group is

trans with regard to the NH₂ group. The other isomers have the terminal CH₃ group in one of two gauche positions and for these conformations we use the labels **g** ($\tau_2 \approx -60^\circ$) and **q** ($\tau_2 \approx +60^\circ$). Note that **Pr-1tg** and **Pr-1tq** are enantiomers and the latter equals **Pr-1tg**'. In the bottom row of Scheme 1-5 are shown the derivatives of **Et-1g** and the three structures **Pr-1gg**, **Pr-1gt** and **Pr-1gq** are unique and asymmetric rotamer structures. Overall, one needs to search for five unique structures of **Pr-1** and nine local minima enter the Boltzmann analysis. All five structures were located and molecular models of the optimized structures are shown in Figure 1-3.

Figure 1-3. Optimized structures of propylamine conformers. The number in parentheses is the population percentage from to the Boltzmann analysis at 298 K for a single unique enantiomer.

Replacement of H_a with a carboxyl group in the structures of propylamine in the first row of Scheme 1-5 affords the carbamic acid structures in the first row of Scheme 1-6. In contrast to **Pr-1**, all three structures **Pr-2tg**, **Pr-2tt**, and **Pr-2tq** are unique asymmetric structures.

Replacement of either H_b or H_a in the structures of propylamine in the second row of Scheme 1-5 affords the carbamic acid structures on the second and third rows of Scheme 1-6. However, because of the planarization at the N atom, some of the **Pr-2c** and **Pr-2h** structures are not unique. For example, **Pr-2cg** and **Pr-2cq** would be enantiomers as well as **Pr-2hg** and **Pr-2hq**. Overall, we expected up to seven unique structures of **Pr-2** and, in addition, an equal number of unique structures of **Pr-3**. However, not all of these structures correspond to stationary structures on the potential energy surface.

1.3.2.2. Models of Local Minima

The structures **Pr-2t** and **Pr-2c** are shown in the top two rows of Figure 1-4. With the exception of **Pr-2ct**, all of these structures were located as local minima. In the bottom two rows structures of types **Pr-3t** and **Pr-3c** are shown and with the exception of **Pr-3ct**, all of these were also located as local minima. As in the case of the ethyl system, none of the **Pr-Xh** conformations

Figure 1-4. Optimized structures of propylcarbamic acid **Pr-2** (top) and **Pr-3** (bottom). The number in parentheses is the population percentage from the Boltzmann analysis at 298 K for a single unique enantiomer.

could be located. In **Pr-2c** and **Pr-3c** the planarization of the amide N occurs and the large COOH group at N must be staggered between the H atoms of the C(1)H₂ methylene group.

These structures inadvertently contain one near-eclipsed C2–C1–N–H moiety. It is one consequence that **Pr-2cg** and **Pr-2cq** no longer represent different local minima because the enantiomer **Pr-2cg'** equals **Pr-2cq** (Figure 1-4), that is, the conformations about the C1–N and C1–C2 bonds are correlated in **Pr-2cg** and **Pr-2cq**. The same is true for **Pr-3cg** and **Pr-3cq**. In Table 1-1, we chose to list **Pr-2cg** and **Pr-3cg** with degeneracies of two and **Pr-2cq** and **Pr-3cq** are not considered in the Boltzmann analysis. There will be similar cases in the following section and we will apply this convention throughout.

None of the structures **Pr-2h** and **Pr-3h** exist as local minima and no structures of these types appear in Figure 1-4. The planarization at the amide N would place the large COOH group in an eclipsed conformation about the C1–N bond, $\chi \approx 0^\circ$. We happened to locate one C_s -symmetric structure **Pr-2ht** and it is a transition state structure ($\nu = 1103 \text{ cm}^{-1}$) for rotation about the C1–N bond. The energy and structural data for **Pr-2ht** are included in the Appendix.

We located four unique asymmetric structures for **Pr-2** and four unique asymmetric structures and one unique symmetric structure for **Pr-3**. For the reasons given above, the symmetric structure, **Pr-3ct**, was not considered in the Boltzmann analysis. All of the asymmetric structures have enantiomers, so that a total of sixteen propylcarbamic acid conformers were considered in the Boltzmann analysis.

1.3.2.3. Potential Energy Surface for PrNH–COOH Torsion

As with the ethylamine, we investigated the rotation about the dihedral angle $\chi = \angle(\text{HO}_2\text{C}-\text{N}-\text{C1}-\text{C2})$ which connects on the PES the propylcarbamic acid structures with C_s symmetry, namely **Pr-2ct** and **Pr-3ct**, to the structures of type **Pr-2tt** and **Pr-3tt**, respectively. The results were very similar to ethylamine case. The **Pr-2ct** region is very flat. The C_s -

symmetric transition state is slightly more pronounced and the sinks for the surrounding C_1 -local minima, **Pr-2ct**(C_1) and **Pr-2ct'**(C_1), are slightly deeper than those for the ethyl system. Still, they are much too shallow to be considered bound minima, and therefore, **Pr-2ct**(C_1) and its enantiomer are UBMs. In fact, all attempts to locate the minima with the topology of **Pr-2ct** using initial structures with small distortions from the C_s -structure led to a structure of the **Pr-2tt** type. The **Pr-2ct** region is simply a transition state region for the enantiomerization **Pr-2tt** $\rightleftharpoons$ **Pr-2tt'**.

Figure 1-5. PES scans of the dihedral angle $\chi = \angle(\text{HO}_2\text{C}-\text{N}-\text{C1}-\text{C2})$ for the propylcarbamic acids **Pr-2** and **Pr-3**. Plots on the left show the full χ range and plots on the right are close ups of the regions containing **Pr-2c** and **Pr-3c**. Relative E in kcal/mol.

Again, similar to the ethylamine case, the C_s -symmetric **Pr-3ct** is a shallow local minimum on the PES ($\nu_1 = 35 \text{ cm}^{-1}$) and the barrier to rotation about the N–C1 bond is only $\Delta E = 0.36$ kcal/mol. This value is lower than the thermal energy associated with the ν_1 mode of the stationary structure **Pr-3ct** (0.594 kcal/mol). Thus, the stationary structure **Pr-3ct** is also a UBM

and therefore not considered in the Boltzmann analysis. Essentially, the entire **Pr-3c** region is a transition state region for the enantiomerization **Pr-3tt** $\rightleftharpoons$ **Pr-3tt'**.

The sinks around **Pr-2tt** and **Pr-2tt'** are shallow and contain at most two bound vibrational states for the normal mode promoting the rotation about the C1–N bond ($\nu_3 = 101 \text{ cm}^{-1}$). The sinks around **Pr-3tt** and its enantiomer are also shallow, containing at most two bound vibrational states for the normal mode promoting the rotation about the C1–N bond ($\nu_3 = 96 \text{ cm}^{-1}$). Therefore, **Pr-2** is a fluxional molecule with equal populations of **Pr-2tt** and **Pr-2tt'** and **Pr-3** is also a fluxional molecule with equal populations of **Pr-3tt** and **Pr-3tt'**.

1.3.2.4 Relative Energies and Population Analysis

The all-*trans* **Pr-1tt** is the most stable structure as expected. Yet, the *gauche* structure **Pr-1tg** with $\tau_2 = \angle(\text{N-C1-C2-C3}) \approx 60^\circ$ are nearly isoenergetic and, because it is asymmetric and has an enantiomer, *gauche* structures dominate. Structures of the **Pr-1g** type are all significantly higher in energy, but still account for about 13% of the population.

For the propylcarbamic acids, structures with a *gauche* conformation with respect to the C1–C2 bond dominate. **Pr-2tg** is the most stable structure, and is preferred by about 0.2 kcal/mol over the fully *trans* structure. **Pr-2tq** is virtually isoenergetic with **Pr-2tt**. The *gauche* preference persists even when the carbamino group is rotated such that the COOH group is staggered between H_c and H_d and **Pr-2cg** and its enantiomer are the only structures of that type with large contributions to the overall propylcarbamic acid population. In general, we found a strong preference for the conformations with the *trans*-amide bond over the *cis*-amide bond, i.e., **Pr-2** is generally preferred over **Pr-3**. The stability difference of the *trans*-amide structures and *cis*-

amide structures is large enough that all of the **Pr-3** structures combined only account for 11% of the propylcarbamic acid population.

As **Pr-1tt** and **Pr-2tg** are the most stable structures, they are included in Table 1-3. Averaging over all nine propylamine minima, the average energy of propylamine at room temperature is increased by 0.31 kcal/mol from its most stable structure. Averaging over all sixteen propylcarbamic acids, the energy is increased by 0.30 kcal/mol from its most stable structure. Both averaged molecules have increased energies of approximately the same amount such that the thermochemistry of reaction using the Boltzmann averages is virtually unchanged from the thermochemistry using the most stable structures. Put another way, because both the propylamine and the propylcarbamic acid have several available low-lying minima, the distributions of the molecules are readily able to adjust to temperature, and therefore, the energy available at room temperature is easily tolerated by a simple change in the species distributions for both molecules.

1.3.3. Enumeration of Conformations of Butylamine and N-Butylcarbamic Acid

1.3.3.1. Possible Structures

The investigated conformers of butylamine are shown in Scheme 1-7. For the butyl systems, an extra label is required to distinguish the conformations. As before, the first label refers to the conformation about the N–C1 bond and the second label refers to the conformation about

Scheme 1-7. Investigated Conformations of Butylamine

Bu-1tgg

Bu-1tgt

Bu-1tgq

Bu-1ttg

Bu-1ttt

Bu-1ttq = Bu-1ttg'

Bu-1tqg = Bu-1tqg'

Bu-1tgt = Bu-1tgt'

Bu-1tqq = Bu-1tgg'

Bu-1ggg

Bu-1ggt

Bu-1ggq

Bu-1gtg

Bu-1gtt

Bu-1gtq

Bu-1gqg

Bu-1gqt

Bu-1gqq

the C1–C2 bond. The third and new label describes the conformation about the C2–C3 bond and the structures shown feature dihedral angles $\tau_3 = \angle(\text{C1}–\text{C2}–\text{C3}–\text{C4})$ that are either *trans* (**t**, $\tau_3 \approx 180^\circ$) or *gauche* (**g**, $\tau_3 \approx -60^\circ$; **q**, $\tau_3 \approx +60^\circ$). Each butylamine conformation can be thought of as a derivative of a propylamine where one of the terminal H atoms is replaced by a methyl group.

Thus, there are three butylamine conformations for every parent propylamine conformation. In Scheme 1-7, the first two descriptions are the same in each row (i.e., **Bu-1tg** in row 1, **Bu-1tt** in row 2, etc.) Of course, not all of the conformations are unique and many more pairs of enantiomers are expected for the butyl system. For example, the extension of the carbon chains of the pair of enantiomers **Pr-1tg** (row 1) and **Pr-1tq** (row 3) does not lead to six new and unique trial structures because **Bu-1tqg = Bu-1tgg'**, **Bu-1tqq = Bu-1tgg'**, **Bu-1tqt = Bu-1tgt'**. In such cases, we always consider the trial structure that appears first in the scheme. Total, we expect up to 14 unique structures of butylamine, one symmetric conformation (**Bu-1ttt**) and 13 asymmetric conformations, which would yield a maximum of 27 conformers for the Boltzmann statistical analysis. All 14 unique structures were located they are shown in Figure 1-6.

Figure 1-6. Optimized structures of butylamine conformers **Bu-1t** (top) and **Bu-1g** (bottom).

The potential butylcarbamic acid structures are enumerated in Scheme 1-8. The top three rows of the butylcarbamic acid trial structures in Scheme 1-8 correspond to the butylamine structures in

Scheme 1-7 where H_a has been replaced by COOH. All nine of the **Bu-2t** type structures are unique and asymmetric. Replacement of H_b or H_a in the **Bu-1g** type structures with COOH yields nine trial structures of **Bu-2c** and nine structures of **Bu-2h**. Further, we expected the same number of conformations and with the same symmetry for the **Bu-3t**, **Bu-3c** and **Bu-3h** trial structures. Thus, there are 27 unique trial structures for each of **Bu-2** and **Bu-3** (Table 1-1).

Scheme 1-8. Investigated Conformations of Butylcarbamic Acids

Bu-2tgg

Bu-2tgt

Bu-2tgq

Bu-2ttg

Bu-2ttt

Bu-2ttq

Bu-2tqg

Bu-2tqt

Bu-2tqq

Bu-2cgg

Bu-2cgt

Bu-2cgq

Bu-2ctg

Bu-2ctt

Bu-2ctq

Bu-2cqg

Bu-2cqt

Bu-2cqq

Bu-2hgg

Bu-2hgt

Bu-2hgg

Bu-2htg

Bu-2htt

Bu-2htq

Bu-2hqg

Bu-2hqt

Bu-2hqq

1.3.3.2. Models of Local Minima

Not all of the possible conformations correspond to stationary structures on the potential energy surface. The molecular models of the conformers that do exist as local minima on the potential energy surface for **Bu-2** are shown in Figure 1-7 and for **Bu-3** in Figure 1-8.

Figure 1-7. Optimized structures of the **Bu-2t** type (top) and **Bu-2c** type (bottom) of butylcarbamic acid conformers.

None of the **Bu-2h** conformations could be located as stationary structures; because of steric problems between the COOH group and the C2 methylene group in any structure with $\chi \approx 0^\circ$.

Only three structures of the **Bu-2c** conformations ($\chi \approx 180^\circ$) could be located as unique minima, but many of the **Bu-2c** type trial structures would rotate about χ during optimization and yield

structures of the **Bu-2t** type. Attempts to locate a structure of type **Bu-2cgg**, for example, led to the minimum of type **Bu-2tqq**. As with the propyl systems, in some types of trial structures the dihedral angles about the C1–N and the C1–C2 bonds are correlated and we deal with these situations in the same way as before. For example, we recognize that the structure **Bu-2ctq** is the enantiomer of **Bu-2ctg** and, hence, we consider the enantiomers **Bu-2ctg** and **Bu-2ctg'** (but not **Bu-2ctq** and **Bu-2ctq'**). The same is true for the types **Bu-2cgt** and **Bu-2cqt**.

Bu-3tgg (0.3%)

Bu-3tgt (1.3%)

Bu-3tgq (0.1%)

Bu-3ttg (0.5%)

Bu-3ttt (1.5%)

Bu-3ttq (0.3%)

Bu-3tqg (0.1%)

Bu-3tgt (1.1%)

Bu-3tqq (0.5%)

Bu-3cgg (0.3%)

Bu-3cgt (0.3%)

Bu-3cgq (0.0%)

Bu-3ctg (0.3%)

Bu-3ctt (0%)

Bu-3ctq = Bu-3ctg'(enant.)

Bu-3cqg = Bu-3cgq' (enant.)

Bu-3cqt = Bu-3cgt' (enant.)

Bu-3cqq = Bu-3cgg' (enant.)

Figure 1-8. Optimized structures of the **Bu-3t** type (top) and **Bu-3c** type (bottom) conformers of butylcarbamic acid.

Interestingly, all **Bu-3t** and **Bu-3c** structures were found to exist as local minima, with the exception of **Bu-3ctt** which of course is a transition state. As with the ethyl and propyl systems, these *cis*-amide structures are generally much higher energy than the analogous *trans*-amide (**Bu-2**) structures. Similar to the **Bu-2t** structures, the most stable **Bu-3t** structures are those with the *trans* configuration about the C2–C3 bond ($\tau_3 \approx 180^\circ$).

1.3.3.3. Potential Energy Surface for the BuNH–COOH Torsion

We also computed the C_s -symmetric structure for **Bu-2ctt** (C_s) and it is a transition state structure ($\nu_1 = i23.47\text{ cm}^{-1}$). Since the barrier between **Bu-2ctt**(C_1) and **Bu-2ctt'**(C_1) is very small, they can be considered to be just one fluxional structure of type **Bu-2ctt**.

Figure 1-9. PES scans of the dihedral angle $\chi = \angle(\text{HO}_2\text{C}-\text{N}-\text{C1}-\text{C2})$ for the propylcarbamic acids **Bu-2** and **Bu-3**. Plots on the left show the full χ range and plots on the right are close ups of the regions containing **Bu-2c** and **Bu-3c**. Relative E in kcal/mol.

But, the rotational barrier between **Bu-2ctt** and **Bu-2ttt** is also very low, and therefore, even the fluxional structure of **Bu-2ctt** is not a real minimum on the potential energy surface (Figure 1-9). This is complicated by the fact that on the *G* surface, **Bu-2ctt**(*C*₁) was found to be very stable. This called for some further investigation the thermochemistry of **Bu-2ctt** and **Bu-2ttt**. Because the potential energy well of **Bu-2ctt** is shallow, the contribution of the first fundamental frequency to the total entropy was drastically overestimated, thereby lowering the Gibbs free energy. Recalculation of relative free energy after removing the contribution from the thermochemical contributions from the first frequency, we found the $\Delta(G-G(\nu_1))$ to be much more similar to the ΔE for the two conformers. Table 1-4 below summarizes the thermochemistry for these conformers both with and without the contribution from ν_1 . Thus, we can conclude that **Bu-2ctt** is not a true minimum on either the *G* or *E* surface.

Table 1-4. Energy Values for the **Bu-2ttt** to **Bu-2ctt** Transition

	<i>E</i>	<i>S</i>	<i>S</i> - <i>S</i> (ν_1)	<i>G</i>	<i>G</i> - <i>G</i> (ν_1)
Bu-2ttt	-402.177264	96.23	91.74	-402.046920	-402.044784
Bu-2ctt	-402.175890	99.27	92.26	-402.047023	-402.043692
$\Delta(2ttt \rightarrow 2ctt)$	+0.862			-0.065	+0.685

S in cal/mol, *E* and *G* in Hartrees, and ΔE and ΔG in kcal/mol.

1.3.3.4. Relative Energies and Population Analysis

All of the unique butylamine trial structures exist as local minima on the potential energy surface. Of the **Bu-1t** structures, the most stable are **Bu-1tgt** and **Bu-1ttt** where $\tau_3 \approx 180^\circ$ and they are nearly isoenergetic. **Bu-1tgg** and **Bu-1ttg** are also present in significant amounts at 298 K. **Bu-1tgq**, however, is much higher in energy and has very little contribution to the overall population. The **Bu-1t** structures are generally favored over the **Bu-1g** structures. With the **Bu-1g** structures, we again found that the structures with $\tau_3 \approx 180^\circ$ are the lowest in energy and **Bu-**

1gtt is slightly more favored than **Bu-1ggt** and **Bu-1gqt**. **Bu-1gtg** and **Bu-1gtq**, where $\tau_3 = -60^\circ, +60^\circ$ respectively, are the almost isoenergetic and have the next highest contribution and are only slightly preferred over **Bu-1ggg** and **Bu-1gqq** which also have $\tau_2 = -60^\circ, +60^\circ$ respectively. **Bu-1ggq** and **Bu-1gqg** are the highest energy structures and have very low contributions to the overall population.

All of the **Bu-2t** conformers exist as stationary structures and are shown in the top three rows of Figure 1-7. The **Bu-2t** structures with a *trans* conformation about the C2–C3 bond ($\tau_3 \approx 180^\circ$) are noticeably more stable than those conformers that have τ_3 *gauche*. The most stable structure is **Bu-2ttt** which accounts for 8.4% of the overall population and **Bu-2tgt** and **Bu-2tqt** account for 6.0% and 6.8% respectively. Most of the structures that are *gauche* with respect to τ_3 are essentially isoenergetic and each contribute roughly 3% to the total population with three exceptions. Two exceptions, **Bu-2tgq** and **Bu-2tqg** have the terminal methyl group and the COOH group oriented in the same direction which is sterically disfavored, and therefore, they account for only 1.3% and 0.5% of the total population, respectively. The third exception, **Bu-2tqq** is more stable than the others and accounts for 5.0% of the total population. The only **Bu-2c** type structures found to be stationary structures were **Bu-2cgt** and **Bu-2ctg**; they also have relatively high energy and together account for only 6.1% of the overall population.

The **Bu-3** type structures are shown in Figure 1-8 and totally contribute only 7.5% to the overall population. The relative stabilities of the **Bu-3** type structures follows the same pattern as the **Bu-2** type structures. The most stable of the **Bu-3** type structures is **Bu-3ttt**, which contributes only 1.5 % to the total population. The **Bu-3** structures that did not have an analogous **Bu-2** structure, namely **Bu-3cgg** and **Bu-3cgq** and their enantiomers are very high in energy and so have very little contribution to the Boltzmann analysis.

Table 1-3 lists the Gibbs free energies for the most stable structures of butylamine and butylcarbamic acid, **Bu-1tgt** and **Bu-2ttt**, respectively. Table 1-3 also includes the statistically averaged free energies of these molecules, and the relative energy difference. The reaction free energies for R3 are given in the final row of Table 1-3 for each approximation. Because both the reactants and the products of the reaction are offset by about 0.49 kcal/mol, the reaction thermochemistry is mostly unchanged for this system when using the Boltzmann analysis.

1.3.4. Thermochemistry of the Capture Reaction

Figure 1-10 illustrates the main message of the computed data. The solid lines correspond to the MSS model and the dashed lines give the free energies $G_{\text{rel}}(\mathbf{M})$ calculated with the Boltzmann statistical analysis for the amine ($\mathbf{M} = \mathbf{AM}$) and the carbamic acid ($\mathbf{M} = \mathbf{CA}$). Figure 1-10 shows that an increase in the number of accessible conformers increases the average energy of each system by $\langle G_{\text{rel}}(\mathbf{M}) \rangle$. While it is obvious that the $\langle G_{\text{rel}}(\mathbf{M}) \rangle$ values of amine and carbamic acid should increase, the estimation of that increase is unclear and moreover it is also entirely unclear how these increases affect reaction energies ΔG and the statistical contribution $SC = \Delta G_{\text{MSS}} - \Delta G_{\text{BD}}$.

Figure 1-10. Reaction energy diagrams for the addition of CO₂ to ethyl-, propyl-, and butylamine highlighting the energy differences between the calculated ΔG values calculated using only the most stable structures and those calculated with the full ensemble using Boltzmann statistics.

For the ethyl system with its small values of $\langle G_{\text{rel}}(\text{EtNH}_2) \rangle = 0.27$ kcal/mol and $\langle G_{\text{rel}}(\text{EtNHCOOH}) \rangle = 0.14$ kcal/mol, a significant but small effect on the reaction energy occurs with $SC = 0.13$ kcal/mol. Figure 1-10 shows the qualitatively expected increase of the $\langle G_{\text{rel}}(\mathbf{M}) \rangle$ values for propyl and butyl systems. Unexpected and perhaps also surprising is our finding that the SC values for the propyl (0.01 kcal/mol) and butyl systems (-0.01 kcal/mol) are practically negligible.

Pareto plots were generated to illustrate the distribution of species in conformational space (Figure 1-11). A Pareto plot includes a column graph of the percent contribution of each conformer plotted by decreasing significance on the horizontal axis. The plot also includes a Pareto line that keeps a running total of percentage of conformational space covered by the conformations to the left. In each plot, the range of the primary axis was selected for best resolution and the secondary axis was added for the Pareto line.

Most chemists tend to assume that $\langle G_{\text{rel}}(\mathbf{M}) \rangle$ is somehow related to the number of accessible conformations of $\mathbf{M}$ and also that SC might be related to the difference of accessible conformations of substrate and product. Yet, this assumption is not even true to a first approximation. If Figure 1-11 shows anything, it is that the origin of $\langle G_{\text{rel}}(\mathbf{M}) \rangle$ is intractable. No matter how hard one tries, there is no short-cut to a reasonable estimate of SC . Thus, the most important conclusions to take away from the present study are that $G_{\text{rel}}(\mathbf{M})$ is modest for every molecule and that SC is entirely negligible at room temperature for the propyl and butyl systems.

1.4. Conclusion

The Boltzmann-averaged free energies of the capture reaction are compelling evidence that suggest the small alkylamine systems are good candidates for reversible CO_2 capture. The ΔG values near -3.0 kcal/mol are in excellent agreement with experimental values measured by NMR spectroscopy.²⁴ The difference between the values calculated with the most stable structure and those calculated with the Boltzmann analysis differ at most by 0.07 kcal/mol.

One major purpose of this study was to investigate the role of different conformational states on the entropy and the free energy of the capture reaction. From the results, it seems that the conformation of the alkylamine has very little effect on the overall capture reaction and the loss of rotational freedom by the addition of the CO_2 has a very little effect on the reaction free energy. However, this may not be the case for the tetrapeptide or for the rubisco enzyme, because of the presence of the carboxylic acid groups and the Mg^{2+} ion.

1.5. References

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1.6 Appendix

Table 1-5. Thermodynamic Data and Relative Energies^a of Carbamic Acid Conformers

Species	Energy	VZPE	TE	<i>S</i>	ΔE_{rel}	ΔG_{rel}	<i>P_i</i>
CO ₂	-188.486130	7.31	8.96	51.08		0.00	100.0
<hr/> Ethylcarbamic acid <hr/>							
Et-2t (2)	-323.599603	68.11	72.38	81.16	0.00	0.00	44.4
Et-2c (UBM)	-323.598561	68.12	72.43	81.13	0.65	0.71	-
Et-2c (TS) <i>C_s</i>	-323.598489	67.77	71.69	78.32	0.73	0.88	-
Et-2h	DNE						
Et-3t (2)	-323.597835	68.11	72.33	80.63	1.11	1.22	5.6
Et-3c (UBM) <i>C_s</i>	-323.596871	67.96	72.33	82.93	1.72	1.14	-
Et-3h	DNE						
<hr/> Propylcarbamic acid <hr/>							
Pr-2tg (2)	-362.888855	86.15	91.19	88.67	0.00	0.00	15.0
Pr-2tt (2)	-362.888645	86.13	91.21	88.48	0.13	0.21	10.5
Pr-2tq (2)	-362.889310	86.27	91.23	87.17	-0.29	0.20	10.7
Pr-2cg (2)	-362.887201	85.95	91.12	90.78	1.04	0.34	8.4
Pr-2ct (UBM)	DNE						
Pr-2ct (TS) <i>C_s</i>	-362.887182	85.72	90.48	85.98	1.05	1.15	-
Pr-2cq	enant.						
Pr-2hg	DNE						
Pr-2ht (TS)	-362.880835	85.91	90.52	84.25	5.03	5.68	-
Pr-2hq	DNE						
Pr-3tg (2)	-362.887065	86.27	91.22	87.79	1.12	1.42	1.4
Pr-3tt (2)	-362.886908	86.01	91.08	88.31	1.22	1.22	1.9
Pr-3tq (2)	-362.887363	86.16	91.10	86.81	0.94	1.40	1.4
Pr-3cg (2)	-362.885624	85.99	91.10	89.31	2.03	1.75	0.8
Pr-3ct (UBM) <i>C_s</i>	-362.885646	86.01	91.20	90.42	1.97	1.45	-
Pr-3cq	enant.						
Pr-3hg	DNE						
Pr-3ht	DNE						
Pr-3hq	DNE						
<hr/> Butylcarbamic acid <hr/>							
Bu-2tgg (2)	-402.177507	104.36	110.07	94.15	-0.15	0.65	2.8
Bu-2tgt (2)	-402.177630	104.25	110.05	95.33	-0.23	0.20	6.0
Bu-2tgq (2)	-402.175674	104.30	110.07	96.42	1.00	1.12	1.3
Bu-2ttg (2)	-402.176509	104.11	110.00	96.26	0.47	0.57	3.2
Bu-2ttt (2)	-402.177264	103.95	109.89	96.23	0.00	0.00	8.4
Bu-2ttq (2)	-402.176427	104.04	109.95	96.33	0.53	0.55	3.3
Bu-2tqg (2)	-402.175565	104.29	110.06	94.85	1.07	1.65	0.5
Bu-2tqt (2)	-402.178021	104.16	109.95	94.44	-0.48	0.12	6.8
Bu-2tqq (2)	-402.178203	104.33	110.05	93.74	-0.59	0.31	5.0

Bu-2cgg	DNE						
Bu-2cgt (2)	-402.175997	104.00	109.95	96.76	0.80	0.70	2.6
Bu-2cqq	DNE						
Bu-2ctg (2)	-402.175344	103.95	109.96	98.79	1.20	0.51	3.5
Bu-2ctt (UBM)	-402.175890	103.78	109.87	99.27	0.86	-0.06	-
Bu-2ctt (TS) C_s	-402.175885	104.85	109.74	89.94	0.83	1.11	-
Bu-2ctq	enant.						
Bu-2cqq	DNE						
Bu-2cqt	enant.						
Bu-2cqq	DNE						
Bu-2hgg	DNE						
Bu-2hgt	DNE						
Bu-2hgq	DNE						
Bu-2htg	DNE						
Bu-2htt	DNE						
Bu-2htq	DNE						
Bu-2hqg	DNE						
Bu-2hqt	DNE						
Bu-2hqq	DNE						
Bu-3tgg (2)	-402.175791	104.45	110.11	93.42	0.92	1.98	0.3
Bu-3tgt (2)	-402.175806	104.10	109.92	95.65	0.91	1.12	1.3
Bu-3tgg (2)	-402.174234	104.32	110.05	94.21	1.90	2.67	0.1
Bu-3ttg (2)	-402.174746	104.05	109.92	96.06	1.58	1.66	0.5
Bu-3ttt (2)	-402.175484	103.89	109.80	96.18	1.12	1.04	1.5
Bu-3ttq (2)	-402.174732	104.19	110.00	95.17	1.59	2.01	0.3
Bu-3tqg (2)	-402.173926	104.11	109.88	94.08	2.09	2.73	0.1
Bu-3tgt (2)	-402.176058	104.03	109.84	94.61	0.76	1.19	1.1
Bu-3tqq (2)	-402.175940	104.23	109.95	93.59	0.83	1.67	0.5
Bu-3cgg (2)	-402.174193	104.13	109.95	95.93	1.93	2.08	0.3
Bu-3cgt (2)	-402.174400	104.05	109.94	95.92	1.80	1.94	0.3
Bu-3cqq (2)	-402.172273	104.12	109.97	95.89	3.13	3.31	0.0
Bu-3ctg (2)	-402.173687	103.96	109.92	97.00	2.24	2.04	0.3
Bu-3ctt (UBM) C_s	-402.174294	103.79	109.87	98.36	1.83	1.17	-
Bu-3ctq	enant.						
Bu-3cqq	enant.						
Bu-3cqt	enant.						
Bu-3cqq	enant.						
Bu-3hgg	DNE						
Bu-3hgt	DNE						
Bu-3hgq	DNE						
Bu-3htg	DNE						
Bu-3htt	DNE						
Bu-3htq	DNE						
Bu-3hqg	DNE						
Bu-3hqt	DNE						
Bu-3hqq	DNE						

a) E given in Hartrees, TE given in kcal/mol, S given in cal mol⁻¹ K⁻¹, ΔG_{rel} given in kcal/mol and P_i is the percentage of molecules that exist as that conformer according to the Boltzmann statistics. A (2) behind the conformer descriptor indicates that the structure has an enantiomer that is included in the Boltzmann analysis. DNE suggests that a stationary structure for that conformer could not be located.

Ethylamine Structures

Et-1t

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.223833	-0.263003	-0.000001
2	1	0	1.265135	-0.908120	-0.885063
3	1	0	1.265199	-0.908001	0.885142
4	1	0	2.124606	0.361578	-0.000076
5	6	0	-0.044845	0.577737	0.000002
6	1	0	-0.051783	1.237272	0.874401
7	1	0	-0.051788	1.237237	-0.874421
8	7	0	-1.294555	-0.185040	0.000005
9	1	0	-1.281720	-0.806523	-0.804648
10	1	0	-1.281688	-0.806565	0.804625

Et-1g

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.241916	-0.234128	-0.024646
2	1	0	1.322603	-0.763160	-0.979637
3	1	0	1.291817	-0.981229	0.775770
4	1	0	2.114295	0.418387	0.078401
5	6	0	-0.050017	0.556367	0.050117
6	1	0	-0.079683	1.115409	0.998188
7	1	0	-0.070162	1.304841	-0.748872
8	7	0	-1.206503	-0.326623	-0.127591
9	1	0	-1.231846	-0.969515	0.659388
10	1	0	-2.052897	0.228195	-0.042928

Ethylcarbamic Acid Structures

Et-2t

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.148877	0.208940	-0.656255
2	1	0	-2.263347	-0.621738	-1.358926
3	1	0	-1.610503	1.014766	-1.163474
4	1	0	-3.147530	0.576873	-0.401906
5	6	0	-1.408449	-0.233651	0.594808
6	1	0	-1.309335	0.595362	1.298172
7	1	0	-1.956015	-1.023891	1.112112
8	7	0	-0.075966	-0.743608	0.318797
9	1	0	0.013481	-1.693538	-0.009442
10	6	0	0.944239	0.093866	0.066471
11	8	0	2.034115	-0.573860	-0.386036
12	1	0	2.735773	0.072755	-0.533245
13	8	0	0.934355	1.307577	0.235409

Et-2c(C_s) (TS) Et-2c_Cs_01.log

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.275555	1.307367	-0.000000
2	1	0	2.091277	1.922035	0.886324
3	1	0	2.091277	1.922035	-0.886324
4	1	0	3.331146	1.025995	-0.000000
5	6	0	1.405021	0.068012	0.000000
6	1	0	1.615483	-0.548766	-0.879609
7	1	0	1.615483	-0.548766	0.879609
8	7	0	-0.000000	0.440662	-0.000000
9	1	0	-0.256557	1.415889	-0.000000
10	6	0	-0.966561	-0.484604	0.000000
11	8	0	-2.202539	0.076013	-0.000000
12	1	0	-2.850488	-0.640023	0.000000
13	8	0	-0.787675	-1.698224	0.000000

Et-2c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.596762	-0.284886	-0.134216
2	1	0	2.588362	-0.698060	-1.146866
3	1	0	2.732573	-1.110934	0.571185
4	1	0	3.464269	0.373406	-0.044690
5	6	0	1.323665	0.482690	0.157251
6	1	0	1.375201	0.943717	1.150454
7	1	0	1.186562	1.291403	-0.564488
8	7	0	0.174400	-0.402518	0.077102
9	1	0	0.311310	-1.393567	0.206116
10	6	0	-1.078024	0.064196	-0.006538
11	8	0	-1.984441	-0.946126	-0.011145
12	1	0	-2.863667	-0.552883	-0.072202
13	8	0	-1.399287	1.245194	-0.081130

Et-3t

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.109728	0.263797	0.634855
2	1	0	2.261706	-0.531027	1.371133
3	1	0	1.549481	1.071085	1.114308
4	1	0	3.091981	0.655100	0.352817
5	6	0	1.375383	-0.259742	-0.588745
6	1	0	1.251299	0.528145	-1.333404
7	1	0	1.947259	-1.056694	-1.068158
8	7	0	0.062912	-0.812375	-0.282883
9	1	0	0.013455	-1.770627	0.027295
10	6	0	-1.030567	-0.081954	0.001139
11	8	0	-2.086732	-0.535349	0.430443
12	8	0	-0.861577	1.232664	-0.266723
13	1	0	-1.696362	1.679519	-0.077061

Et-3c(C_s) (UBM)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.347203	1.142183	-0.000000
2	1	0	2.221093	1.771119	0.886446
3	1	0	2.221093	1.771119	-0.886446
4	1	0	3.371835	0.763162	0.000000
5	6	0	1.364645	-0.010904	0.000000
6	1	0	1.518033	-0.642239	-0.880319
7	1	0	1.518033	-0.642239	0.880319
8	7	0	-0.000000	0.499386	-0.000000
9	1	0	-0.146943	1.496856	-0.000000
10	6	0	-1.108360	-0.254049	-0.000000
11	8	0	-2.258882	0.174797	-0.000000
12	8	0	-0.823858	-1.577343	0.000000
13	1	0	-1.662161	-2.056487	0.000000

Propylamine Structures

Pr-1tg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.651530	0.646237	-0.295934
2	1	0	0.566207	0.688921	-1.390661
3	6	0	-0.750621	0.579263	0.308297
4	1	0	-0.674017	0.579905	1.401784
5	1	0	-1.302782	1.486917	0.042249
6	7	0	-1.568013	-0.572677	-0.080648
7	1	0	-1.588985	-0.617607	-1.096157
8	1	0	-1.091593	-1.421216	0.209584
9	6	0	1.537610	-0.525174	0.109649
10	1	0	1.634899	-0.586890	1.199506
11	1	0	1.133545	-1.480994	-0.239080
12	1	0	2.545341	-0.431540	-0.306672
13	1	0	1.122366	1.589286	0.011908

Pr-1tt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.526939	0.523850	0.000003
2	1	0	-0.409459	1.172469	-0.878685
3	1	0	-0.409462	1.172463	0.878695
4	6	0	0.590299	-0.513398	0.000000
5	1	0	0.482394	-1.164580	0.874996
6	1	0	0.482387	-1.164584	-0.874992
7	7	0	1.952305	0.024067	-0.000004
8	1	0	2.047278	0.637729	-0.804928
9	6	0	-1.911118	-0.112206	-0.000001
10	1	0	-2.705819	0.640018	0.000010
11	1	0	-2.057101	-0.744571	-0.882568
12	1	0	-2.057097	-0.744593	0.882550
13	1	0	2.047292	0.637706	0.804936

Pr-1gg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.666554	0.650819	-0.278488
2	1	0	0.607080	0.725496	-1.371941
3	6	0	-0.742655	0.573686	0.289275
4	1	0	-0.682178	0.562307	1.390041
5	1	0	-1.289426	1.483092	0.019834
6	7	0	-1.484216	-0.570063	-0.250376
7	1	0	-1.076628	-1.421926	0.123382
8	1	0	-2.427055	-0.545089	0.125367
9	6	0	1.542711	-0.534328	0.113040
10	1	0	1.589449	-0.648455	1.201996
11	1	0	1.168980	-1.475860	-0.302011
12	1	0	2.567898	-0.410585	-0.249404
13	1	0	1.131738	1.580400	0.072403

Pr-1gt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.542862	0.523555	-0.061433
2	1	0	-0.454259	1.088008	-0.998037
3	1	0	-0.428335	1.254907	0.750478
4	6	0	0.590397	-0.484560	0.015709
5	1	0	0.482108	-1.073620	0.940639
6	1	0	0.498587	-1.195231	-0.813345
7	7	0	1.894181	0.175441	-0.092384
8	1	0	2.017694	0.760191	0.729707
9	6	0	-1.911643	-0.137430	0.029513
10	1	0	-2.720428	0.597132	-0.029408
11	1	0	-2.059978	-0.855925	-0.783968
12	1	0	-2.030238	-0.681691	0.972616
13	1	0	2.620224	-0.531251	-0.024734

Pr-1gq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.661429	0.611349	-0.313043
2	6	0	0.727146	0.563766	0.308633
3	1	0	1.261814	1.493686	0.059664
4	1	0	0.633307	0.544437	1.400611
5	7	0	1.461657	-0.635790	-0.104521
6	1	0	1.636576	-0.565710	-1.103277
7	1	0	2.379169	-0.618655	0.329514
8	1	0	-1.121937	1.573652	-0.057245
9	6	0	-1.571132	-0.527253	0.130802
10	1	0	-1.711085	-0.516783	1.217660
11	1	0	-2.561558	-0.453000	-0.329317
12	1	0	-1.153480	-1.501014	-0.136707
13	1	0	-0.561920	0.606750	-1.407607

Propylcarbamic Acid Structures

Pr-2tg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.844393	-0.718500	0.802321
2	1	0	0.474806	-1.745784	0.818138
3	1	0	1.379395	-0.555500	1.741278
4	7	0	-0.306520	0.169506	0.806712
5	1	0	-0.185465	1.109283	1.152902
6	6	0	-1.343386	-0.044661	-0.022157
7	8	0	-2.195289	1.010049	-0.032943
8	1	0	-2.933539	0.786897	-0.613470
9	8	0	-1.541411	-1.062210	-0.675211
10	6	0	1.776684	-0.502138	-0.384699
11	1	0	2.575635	-1.251232	-0.328249
12	1	0	1.226051	-0.704733	-1.310926
13	6	0	2.373838	0.897980	-0.420716
14	1	0	1.598938	1.664171	-0.523524
15	1	0	2.932590	1.113949	0.496578
16	1	0	3.061645	1.017606	-1.262968

Pr-2tt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.655573	-0.051673	0.562189
2	1	0	1.668959	-0.853951	1.309716
3	1	0	1.181788	0.814802	1.038126
4	6	0	0.805311	-0.488653	-0.623751
5	1	0	0.774020	0.302452	-1.376992
6	1	0	1.242445	-1.367436	-1.103880
7	7	0	-0.562084	-0.821705	-0.268833
8	1	0	-0.760376	-1.741380	0.094720
9	6	0	-1.473662	0.140861	-0.053601
10	8	0	-2.629186	-0.369116	0.439987
11	1	0	-3.252064	0.360625	0.548196
12	8	0	-1.323651	1.334911	-0.286442
13	6	0	3.073953	0.293030	0.131030
14	1	0	3.687048	0.606456	0.980837
15	1	0	3.568756	-0.566694	-0.333364
16	1	0	3.079659	1.109304	-0.599088

Pr-2tq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.938740	-1.004626	0.519511
2	1	0	-0.795834	-0.592813	1.520219
3	1	0	-1.202476	-2.058444	0.639920
4	7	0	0.341792	-0.939326	-0.162023
5	1	0	0.425634	-1.402016	-1.055274
6	6	0	1.248759	0.012219	0.117300
7	8	0	2.251876	0.017801	-0.796175
8	1	0	2.884259	0.698314	-0.533873
9	8	0	1.226545	0.775366	1.075465
10	6	0	-2.050508	-0.262079	-0.213634
11	1	0	-2.984312	-0.430262	0.336531
12	1	0	-2.191227	-0.716220	-1.202789
13	6	0	-1.790314	1.231600	-0.358321
14	1	0	-1.655983	1.709186	0.617301
15	1	0	-0.890896	1.429449	-0.949816
16	1	0	-2.624255	1.730066	-0.861518

Pr-2cg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.777500	0.859197	-0.259641
2	1	0	-0.685140	1.314991	0.730477
3	1	0	-0.597491	1.650317	-0.996651
4	6	0	-2.169981	0.277781	-0.440867
5	7	0	0.237414	-0.172680	-0.384742
6	1	0	0.007576	-1.037769	-0.849752
7	6	0	1.493779	0.016087	0.035811
8	8	0	1.920435	1.029544	0.579447
9	8	0	2.271897	-1.069406	-0.206720
10	1	0	3.158651	-0.874213	0.120774
11	1	0	-2.878953	1.112679	-0.435878
12	1	0	-2.245934	-0.180108	-1.435494
13	6	0	-2.548168	-0.732037	0.635260
14	1	0	-3.574587	-1.086178	0.502134
15	1	0	-1.896814	-1.610962	0.618906
16	1	0	-2.476645	-0.287268	1.633485

Pr-2ct(C_s) (TS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.286916	-0.233912	-0.000000
2	1	0	-4.168774	0.412714	-0.000027
3	1	0	-3.348876	-0.877843	0.883323
4	1	0	-3.348867	-0.877905	-0.883279
5	6	0	-2.002182	0.581774	-0.000022
6	1	0	-1.971642	1.236383	-0.879669
7	1	0	-1.971659	1.236455	0.879572
8	6	0	-0.778499	-0.316286	0.000026
9	1	0	-0.788911	-0.968579	-0.880061
10	1	0	-0.788933	-0.968513	0.880162
11	7	0	0.438393	0.476037	0.000005
12	1	0	0.377390	1.482471	0.000041
13	6	0	1.645555	-0.100771	-0.000002
14	8	0	2.644293	0.818039	0.000001
15	8	0	1.854519	-1.309633	-0.000013
16	1	0	3.483282	0.340486	-0.000005

Pr-2ht (TS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.856369	0.905763	-0.000000
2	1	0	-1.175845	1.479198	0.877289
3	1	0	-1.175845	1.479198	-0.877290
4	6	0	-1.575625	-0.434375	0.000000
5	7	0	0.604851	0.886512	0.000000
6	1	0	1.048255	1.792655	-0.000001
7	6	0	1.440277	-0.160182	0.000000
8	8	0	1.166418	-1.354015	-0.000000
9	8	0	2.734654	0.274602	0.000000
10	1	0	3.299683	-0.507843	0.000000
11	1	0	-1.286081	-1.018838	-0.877739
12	1	0	-1.286081	-1.018838	0.877740
13	6	0	-3.081563	-0.202407	0.000000
14	1	0	-3.626502	-1.150634	-0.000000
15	1	0	-3.400219	0.361011	0.883344
16	1	0	-3.400219	0.361012	-0.883343

Pr-3tg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.804950	-0.667227	0.848949
2	1	0	0.401943	-1.677788	0.932310
3	1	0	1.364409	-0.472030	1.767402
4	7	0	-0.309276	0.272100	0.832751
5	1	0	-0.128665	1.214571	1.143287
6	6	0	-1.381214	0.166433	0.023835
7	8	0	-2.208192	1.052413	-0.164803
8	8	0	-1.484900	-1.054506	-0.546869
9	6	0	1.724327	-0.548680	-0.361674
10	1	0	2.498254	-1.320799	-0.273905
11	1	0	1.155562	-0.781738	-1.269301
12	6	0	2.368739	0.825518	-0.482148
13	1	0	1.619164	1.611673	-0.616782
14	1	0	2.948189	1.071265	0.414550
15	1	0	3.047477	0.874538	-1.338686
16	1	0	-2.297480	-1.063924	-1.068528

Pr-3tt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.616125	-0.059057	0.560979
2	1	0	1.648542	-0.863183	1.305964
3	1	0	1.125024	0.794962	1.041264
4	6	0	0.775306	-0.514106	-0.624995
5	1	0	0.735850	0.267383	-1.386761
6	1	0	1.229174	-1.388972	-1.096852
7	7	0	-0.586663	-0.882641	-0.269883
8	1	0	-0.749178	-1.815200	0.077629
9	6	0	-1.566680	-0.006947	0.017756
10	8	0	-2.657368	-0.304299	0.494547
11	8	0	-1.239414	1.264415	-0.306367
12	6	0	3.026124	0.318232	0.129274
13	1	0	3.633284	0.640751	0.979961
14	1	0	3.538988	-0.528169	-0.339917
15	1	0	3.013046	1.138112	-0.596705
16	1	0	-1.999088	1.823140	-0.098918

Pr-3tq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.909541	-0.976405	0.571758
2	1	0	-0.732932	-0.518787	1.545443
3	1	0	-1.187469	-2.017477	0.755411
4	7	0	0.348314	-0.982586	-0.161120
5	1	0	0.368747	-1.499575	-1.027978
6	6	0	1.320648	-0.056678	-0.065683
7	8	0	2.257712	0.052111	-0.850989
8	8	0	1.196279	0.736589	1.021983
9	6	0	-2.031344	-0.257597	-0.169825
10	1	0	-2.951104	-0.380181	0.414963
11	1	0	-2.206567	-0.764959	-1.127081
12	6	0	-1.755522	1.221120	-0.406117
13	1	0	-1.597432	1.752662	0.537492
14	1	0	-0.865637	1.373269	-1.025126
15	1	0	-2.593095	1.700507	-0.921562
16	1	0	1.949920	1.340396	1.027539

Pr-3cg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.719237	-0.821462	-0.182545
2	1	0	0.658549	-1.244980	0.824757
3	1	0	0.445611	-1.614941	-0.885430
4	6	0	2.134836	-0.342178	-0.458382
5	7	0	-0.227262	0.280036	-0.296908
6	1	0	0.099367	1.168720	-0.644044
7	6	0	-1.536810	0.209254	-0.022593
8	8	0	-1.901582	-1.020051	0.410665
9	8	0	-2.337932	1.132550	-0.139308
10	1	0	2.782562	-1.225198	-0.475063
11	1	0	2.181268	0.089789	-1.466126
12	6	0	2.652028	0.656462	0.570087
13	1	0	3.691682	0.928655	0.366053
14	1	0	2.071282	1.583897	0.576021
15	1	0	2.610636	0.235857	1.580347
16	1	0	-2.849751	-0.994492	0.591593

Pr-3ct (UBM)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.356338	-2.263484	-0.000000
2	1	0	-3.446571	-2.348098	-0.000000
3	1	0	-1.983555	-2.792159	0.883323
4	1	0	-1.983555	-2.792159	-0.883323
5	6	0	-1.914064	-0.807357	-0.000000
6	1	0	-2.317116	-0.290850	-0.879757
7	1	0	-2.317116	-0.290850	0.879757
8	6	0	-0.400550	-0.690893	-0.000000
9	1	0	0.013717	-1.192117	-0.880847
10	1	0	0.013717	-1.192117	0.880847
11	7	0	-0.000000	0.708431	0.000000
12	1	0	-0.714580	1.419624	0.000000
13	6	0	1.265434	1.149605	0.000000
14	8	0	1.608290	2.328480	0.000000
15	8	0	2.157401	0.131029	-0.000000
16	1	0	3.042637	0.516410	-0.000000

Butylamine Structures

Bu-1tgg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.061151	1.053792	0.016690
2	1	0	-0.511372	1.718672	-0.733569
3	6	0	-1.161039	0.175220	0.614399
4	1	0	-0.766491	-0.399830	1.457983
5	1	0	-1.940553	0.820052	1.034029
6	7	0	-1.800731	-0.767528	-0.306726
7	1	0	-2.092301	-0.253532	-1.134306
8	1	0	-1.096264	-1.419088	-0.640104
9	6	0	1.090862	0.280103	-0.624938
10	1	0	0.715455	-0.300010	-1.477661
11	1	0	1.803876	0.997593	-1.049123
12	1	0	0.334876	1.706467	0.807514
13	6	0	1.818468	-0.647037	0.342301
14	1	0	1.172282	-1.455733	0.698005
15	1	0	2.688976	-1.113347	-0.129840
16	1	0	2.173797	-0.101012	1.223441

Bu-1tgt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.013661	0.706233	0.229058
2	1	0	-0.035680	0.674022	1.328205
3	6	0	1.430037	0.554196	-0.246019
4	1	0	1.461399	0.618735	-1.339736
5	1	0	2.022696	1.397817	0.123513
6	7	0	2.115252	-0.680155	0.147604
7	1	0	2.030004	-0.780909	1.155799
8	1	0	1.606651	-1.469992	-0.237869
9	6	0	-0.960367	-0.350276	-0.330175
10	1	0	-0.377120	1.703919	-0.054773
11	1	0	-0.913437	-0.330578	-1.427544
12	1	0	-0.621019	-1.349560	-0.030099
13	6	0	-2.398443	-0.147951	0.129140
14	1	0	-2.783594	0.827333	-0.188100
15	1	0	-3.067597	-0.913856	-0.275962
16	1	0	-2.474463	-0.189051	1.221314

Bu-1tgq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.045232	1.026455	0.359006
2	1	0	0.157544	0.825367	1.434197
3	6	0	1.246676	0.421332	-0.377379
4	1	0	1.021413	0.351153	-1.447969
5	1	0	2.095206	1.108637	-0.296668
6	7	0	1.717115	-0.893999	0.072722
7	1	0	1.898293	-0.835665	1.071058
8	1	0	0.960061	-1.562614	-0.015373
9	6	0	-1.329102	0.553736	-0.117009
10	1	0	-2.096876	1.086031	0.459009
11	1	0	0.084671	2.118794	0.252076
12	1	0	-1.469834	0.867194	-1.160290
13	6	0	-1.580789	-0.947219	-0.008035
14	1	0	-0.979565	-1.519359	-0.721443
15	1	0	-1.354483	-1.321793	0.996189
16	1	0	-2.628335	-1.185576	-0.219332

Bu-1ttg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.082958	0.687409	0.267517
2	1	0	-0.098462	0.581813	1.361956
3	6	0	-1.006600	-0.361539	-0.343599
4	1	0	-0.965429	-0.288147	-1.436683
5	1	0	-0.657013	-1.367959	-0.094880
6	7	0	-2.410085	-0.266561	0.066402
7	1	0	-2.445211	-0.341119	1.079743
8	1	0	-2.731157	0.677486	-0.132573
9	6	0	1.359098	0.619754	-0.234787
10	1	0	-0.499658	1.680469	0.049445
11	1	0	1.366229	0.726887	-1.327949
12	1	0	1.913387	1.482604	0.154540
13	6	0	2.087660	-0.661504	0.158661
14	1	0	1.640187	-1.547762	-0.300830
15	1	0	3.137979	-0.633921	-0.148640
16	1	0	2.066539	-0.809148	1.244313

Bu-1ttt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.024677	-0.321997	-0.000085
2	1	0	-0.029054	-0.982362	-0.879088
3	6	0	-1.299495	0.512481	-0.000185
4	1	0	-1.304692	1.172467	0.874679
5	1	0	-1.304756	1.172183	-0.875276
6	7	0	-2.551225	-0.248420	0.000073
7	1	0	-2.539023	-0.870163	-0.804268
8	1	0	-2.539204	-0.869470	0.804957
9	6	0	1.244092	0.523315	0.000148
10	1	0	-0.029185	-0.982375	0.878917
11	1	0	1.239147	1.184958	-0.876214
12	1	0	1.239058	1.184456	0.876876
13	6	0	2.512640	-0.319844	-0.000025
14	1	0	2.558093	-0.966986	-0.882741
15	1	0	3.414910	0.300099	0.000272
16	1	0	2.557923	-0.967592	0.882260

Bu-1ttq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.082957	0.687431	0.267508
2	1	0	0.499636	1.680500	0.049439
3	6	0	1.006598	-0.361499	-0.343641
4	1	0	0.656984	-1.367925	-0.094988
5	1	0	0.965459	-0.288044	-1.436721
6	7	0	2.410072	-0.266577	0.066409
7	1	0	2.731134	0.677513	-0.132379
8	1	0	2.445177	-0.341327	1.079737
9	6	0	-1.359110	0.619757	-0.234762
10	1	0	0.098490	0.581826	1.361946
11	1	0	-1.913412	1.482580	0.154603
12	1	0	-1.366271	0.726928	-1.327920
13	6	0	-2.087631	-0.661533	0.158660
14	1	0	-3.137979	-0.633933	-0.148538
15	1	0	-1.640199	-1.547757	-0.300935
16	1	0	-2.066408	-0.809255	1.244300

Bu-1tqg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.045103	1.026326	-0.359179
2	6	0	1.246756	0.421430	0.377202
3	1	0	2.095186	1.108812	0.296205
4	1	0	1.021591	0.351586	1.447838
5	7	0	1.717278	-0.893971	-0.072485
6	1	0	0.960087	-1.562481	0.015379
7	1	0	1.898961	-0.835866	-1.070746
8	1	0	0.157096	0.824789	-1.434314
9	1	0	0.084591	2.118681	-0.252646
10	6	0	-1.329120	0.553734	0.117308
11	1	0	-2.097020	1.086193	-0.458352
12	1	0	-1.469369	0.866916	1.160710
13	6	0	-1.580937	-0.947202	0.007920
14	1	0	-1.354793	-1.321424	-0.996465
15	1	0	-0.979619	-1.519595	0.721022
16	1	0	-2.628472	-1.185540	0.219260

Bu-1tqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.013661	0.706233	0.229055
2	6	0	-1.430038	0.554199	-0.246019
3	1	0	-2.022696	1.397822	0.123512
4	1	0	-1.461399	0.618734	-1.339737
5	7	0	-2.115254	-0.680150	0.147608
6	1	0	-1.606676	-1.469981	-0.237910
7	1	0	-2.029951	-0.780931	1.155797
8	1	0	0.035685	0.674044	1.328202
9	1	0	0.377128	1.703909	-0.054804
10	6	0	0.960361	-0.350290	-0.330156
11	1	0	0.913420	-0.330640	-1.427529
12	1	0	0.621031	-1.349571	-0.030045
13	6	0	2.398445	-0.147943	0.129130
14	1	0	3.067592	-0.913868	-0.275948
15	1	0	2.783592	0.827327	-0.188160
16	1	0	2.474479	-0.188993	1.221305

Bu-1tqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.061100	1.053733	0.016581
2	6	0	1.161031	0.175306	0.614419
3	1	0	1.940436	0.820250	1.034077
4	1	0	0.766480	-0.399756	1.457993
5	7	0	1.800826	-0.767442	-0.306635
6	1	0	1.096563	-1.419523	-0.639404
7	1	0	2.091751	-0.253640	-1.134560
8	1	0	0.511360	1.718584	-0.733679
9	1	0	-0.335005	1.706455	0.807334
10	6	0	-1.090722	0.279848	-0.625068
11	1	0	-0.715071	-0.300705	-1.477409
12	1	0	-1.803590	0.997132	-1.049830
13	6	0	-1.818586	-0.646817	0.342376
14	1	0	-2.689065	-1.113243	-0.129701
15	1	0	-1.172555	-1.455444	0.698511
16	1	0	-2.174021	-0.100434	1.223266

Bu-1ggg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.039127	1.072448	0.010837
2	1	0	-0.457799	1.746110	-0.748027
3	6	0	-1.159626	0.210513	0.575743
4	1	0	-0.784836	-0.357632	1.440892
5	1	0	-1.947484	0.864859	0.962508
6	7	0	-1.752034	-0.648156	-0.454113
7	1	0	-1.064126	-1.346585	-0.720845
8	1	0	-2.510512	-1.175451	-0.032749
9	6	0	1.123784	0.287804	-0.601494
10	1	0	0.782038	-0.243783	-1.498778
11	1	0	1.877465	1.001922	-0.955221
12	1	0	0.343878	1.711131	0.817994
13	6	0	1.773082	-0.700984	0.360490
14	1	0	1.088094	-1.507839	0.639910
15	1	0	2.657051	-1.167861	-0.085258
16	1	0	2.091781	-0.206466	1.284911

Bu-1ggt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.025921	0.709725	-0.215030
2	1	0	0.053415	0.730873	-1.313016
3	6	0	-1.414837	0.550362	0.243749
4	1	0	-1.444959	0.587701	1.345053
5	1	0	-2.000879	1.405170	-0.108847
6	7	0	-2.028035	-0.665613	-0.300054
7	1	0	-1.600640	-1.469631	0.149458
8	1	0	-3.000523	-0.690120	-0.009440
9	6	0	0.962372	-0.381420	0.296154
10	1	0	0.396315	1.686443	0.124102
11	1	0	0.888708	-0.436842	1.390810
12	1	0	0.639079	-1.359654	-0.081022
13	6	0	2.409767	-0.140668	-0.112920
14	1	0	2.780501	0.811930	0.281197
15	1	0	3.073984	-0.929889	0.253486
16	1	0	2.511897	-0.104674	-1.203120

Bu-1ggq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.018990	1.031917	-0.356757
2	1	0	-0.117965	0.842244	-1.433971
3	6	0	-1.233862	0.437482	0.351457
4	1	0	-1.010664	0.345438	1.427037
5	1	0	-2.070992	1.138376	0.274425
6	7	0	-1.679277	-0.825193	-0.251949
7	1	0	-0.963369	-1.529431	-0.109599
8	1	0	-2.484901	-1.158483	0.269067
9	6	0	1.340514	0.534313	0.138510
10	1	0	2.125602	1.064762	-0.415204
11	1	0	-0.042860	2.122166	-0.236771
12	1	0	1.464675	0.829356	1.189005
13	6	0	1.570199	-0.968133	0.010491
14	1	0	0.925657	-1.540450	0.685515
15	1	0	1.380296	-1.318497	-1.009978
16	1	0	2.602291	-1.232602	0.261916

Bu-1gtg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.070147	0.709255	-0.260842
2	1	0	0.069977	0.673824	-1.358627
3	6	0	0.994465	-0.374593	0.269425
4	1	0	0.920583	-0.399787	1.368977
5	1	0	0.663571	-1.355845	-0.084105
6	7	0	2.364087	-0.167094	-0.208177
7	1	0	2.712509	0.695275	0.201642
8	1	0	2.954494	-0.899600	0.173735
9	6	0	-1.361889	0.608189	0.261326
10	1	0	0.485665	1.688659	0.014752
11	1	0	-1.355644	0.685973	1.356777
12	1	0	-1.931283	1.474208	-0.097742
13	6	0	-2.079185	-0.671633	-0.155738
14	1	0	-1.620775	-1.562051	0.284820
15	1	0	-3.128408	-0.660782	0.156182
16	1	0	-2.060528	-0.797519	-1.244202

Bu-1gtt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.014838	-0.331268	-0.041889
2	1	0	-0.002070	-0.922328	-0.967251
3	6	0	-1.292780	0.486539	0.007514
4	1	0	-1.290292	1.101343	0.921736
5	1	0	-1.307413	1.187666	-0.834392
6	7	0	-2.474482	-0.374355	-0.097561
7	1	0	-2.506225	-0.963052	0.730451
8	1	0	-3.304063	0.208392	-0.038275
9	6	0	1.242732	0.525676	0.041678
10	1	0	-0.017457	-1.056322	0.784931
11	1	0	1.239947	1.254296	-0.779763
12	1	0	1.222290	1.114720	0.967947
13	6	0	2.519553	-0.303004	-0.011488
14	1	0	2.580590	-0.877701	-0.942108
15	1	0	3.414997	0.323861	0.047422
16	1	0	2.563064	-1.018048	0.817339

Bu-1gtq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.068484	0.717934	-0.235920
2	1	0	-0.463540	1.708152	0.024411
3	6	0	-1.008590	-0.333474	0.329411
4	1	0	-0.660918	-1.336958	0.045065
5	1	0	-0.977018	-0.293308	1.424365
6	7	0	-2.388786	-0.077298	-0.096865
7	1	0	-2.426532	-0.183573	-1.107199
8	1	0	-2.979698	-0.819118	0.266342
9	6	0	1.372352	0.594738	0.257668
10	1	0	-0.083433	0.660583	-1.334234
11	1	0	1.943791	1.457736	-0.105449
12	1	0	1.386318	0.665083	1.353592
13	6	0	2.072311	-0.687462	-0.182239
14	1	0	3.126662	-0.686642	0.112345
15	1	0	1.614870	-1.578792	0.256742
16	1	0	2.035466	-0.802501	-1.271445

Bu-1gqg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.056387	-0.988429	0.389401
2	6	0	1.373266	-0.447798	-0.151033
3	1	0	2.195607	-0.949915	0.383513
4	1	0	1.472108	-0.736515	-1.204370
5	7	0	1.466921	1.013085	-0.071921
6	1	0	1.335705	1.285265	0.898424
7	1	0	2.415339	1.289472	-0.306369
8	1	0	-0.029731	-0.732677	1.455751
9	1	0	0.121931	-2.083040	0.352287
10	6	0	-1.207532	-0.534029	-0.348244
11	1	0	-1.992872	-1.285587	-0.198287
12	1	0	-1.009068	-0.522804	-1.428497
13	6	0	-1.743138	0.823995	0.094449
14	1	0	-1.011761	1.614650	-0.082056
15	1	0	-2.662969	1.085838	-0.439691
16	1	0	-1.976632	0.821290	1.165296

Bu-1gqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.023895	0.672261	0.254882
2	6	0	-1.412123	0.550156	-0.232163
3	1	0	-1.993611	1.402479	0.152486
4	1	0	-1.432529	0.632018	-1.325055
5	7	0	-1.997872	-0.742392	0.137243
6	1	0	-2.063826	-0.776072	1.150908
7	1	0	-2.957147	-0.768980	-0.194013
8	1	0	0.043171	0.552600	1.348287
9	1	0	0.374497	1.694289	0.059205
10	6	0	0.988012	-0.321654	-0.383645
11	1	0	0.977015	-0.181346	-1.473068
12	1	0	0.630758	-1.341479	-0.206023
13	6	0	2.409861	-0.171851	0.141032
14	1	0	3.094888	-0.885806	-0.327527
15	1	0	2.801471	0.833577	-0.049735
16	1	0	2.452547	-0.338005	1.223206

Bu-1gqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.032054	1.016793	0.107410
2	6	0	1.133006	0.103367	0.629328
3	1	0	1.861679	0.717675	1.181067
4	1	0	0.719820	-0.602332	1.357421
5	7	0	1.748903	-0.668738	-0.452921
6	1	0	2.187514	-0.014145	-1.094853
7	1	0	2.509684	-1.218925	-0.067171
8	1	0	0.481726	1.755773	-0.570801
9	1	0	-0.369499	1.589355	0.954220
10	6	0	-1.115169	0.305925	-0.610575
11	1	0	-0.728366	-0.210358	-1.496150
12	1	0	-1.816539	1.062848	-0.983561
13	6	0	-1.865446	-0.686025	0.270855
14	1	0	-2.737132	-1.099734	-0.246293
15	1	0	-1.234213	-1.530334	0.564159
16	1	0	-2.223661	-0.209014	1.190298

Butylcarbamic Acid Structures

Bu-2tgg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.191010	-1.036934	0.401189
2	1	0	0.543966	-1.402363	1.206992
3	6	0	0.357531	-0.884019	-0.869084
4	1	0	0.992983	-0.683739	-1.733408
5	1	0	-0.179410	-1.810521	-1.082566
6	7	0	-0.613365	0.196523	-0.798336
7	1	0	-0.284015	1.133881	-0.977222
8	6	0	1.884726	0.248470	0.849131
9	1	0	1.127796	0.993227	1.126318
10	1	0	2.445702	0.039865	1.767821
11	1	0	1.937946	-1.820786	0.221275
12	6	0	2.822866	0.837394	-0.198190
13	1	0	2.282949	1.175464	-1.088564
14	1	0	3.367041	1.701393	0.195551
15	1	0	3.564795	0.100716	-0.525922
16	6	0	-1.706149	0.083241	-0.021417
17	8	0	-2.327123	1.277801	0.138279
18	8	0	-2.133261	-0.955638	0.467145
19	1	0	-3.123032	1.130980	0.664913

Bu-2tgt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.251684	-0.737807	0.341224
2	1	0	0.869297	-0.310116	1.276749
3	6	0	0.086104	-1.306930	-0.458523
4	1	0	0.443011	-1.750998	-1.391076
5	1	0	-0.413607	-2.099400	0.102083
6	7	0	-0.915336	-0.314032	-0.812231
7	1	0	-0.740182	0.282501	-1.606665
8	6	0	2.052838	0.311480	-0.420043
9	1	0	1.909551	-1.568700	0.626930
10	1	0	2.421831	-0.125624	-1.357476
11	1	0	1.394226	1.139874	-0.709114
12	6	0	3.220524	0.851200	0.394762
13	1	0	3.916723	0.051132	0.668926
14	1	0	3.787594	1.606552	-0.158309
15	1	0	2.873241	1.314936	1.324454
16	6	0	-1.794389	0.130482	0.102663
17	8	0	-1.995800	-0.367100	1.204150
18	8	0	-2.482999	1.206532	-0.351442
19	1	0	-3.124515	1.452061	0.326951

Bu-2tgq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.338827	-1.004893	-0.416763
2	1	0	-0.760175	-0.818156	-1.329954
3	6	0	-0.369835	-1.176183	0.750769
4	1	0	-0.912641	-1.224202	1.697843
5	1	0	0.171196	-2.119611	0.647666
6	7	0	0.619002	-0.115557	0.878153
7	1	0	0.364674	0.718026	1.384970
8	6	0	-2.402360	0.078556	-0.245347
9	1	0	-3.080210	0.021662	-1.106076
10	1	0	-1.840976	-1.968644	-0.567859
11	1	0	-3.016988	-0.153935	0.634346
12	6	0	-1.869625	1.505252	-0.132848
13	1	0	-1.407133	1.702124	0.838243
14	1	0	-1.120298	1.715796	-0.903720
15	1	0	-2.677835	2.234387	-0.249000
16	6	0	1.600024	0.012420	-0.031581
17	8	0	2.235500	1.204423	0.086911
18	8	0	1.924246	-0.830756	-0.859388
19	1	0	2.953150	1.221199	-0.559084

Bu-2ttg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.147396	-0.610458	0.603215
2	1	0	-0.788265	0.175203	1.280271
3	6	0	-0.327204	-0.565536	-0.680732
4	1	0	-0.667397	-1.335272	-1.378060
5	1	0	-0.441982	0.394904	-1.185149
6	7	0	1.092532	-0.772046	-0.456984
7	1	0	1.430370	-1.713295	-0.324436
8	6	0	-2.646030	-0.441182	0.362508
9	1	0	-0.958917	-1.567651	1.104670
10	1	0	-2.995749	-1.228427	-0.318572
11	1	0	-3.173671	-0.606688	1.309323
12	6	0	-3.028456	0.927205	-0.192798
13	1	0	-2.625347	1.093658	-1.196132
14	1	0	-4.115147	1.039344	-0.259435
15	1	0	-2.652850	1.731554	0.449348
16	6	0	1.875555	0.231707	-0.028127
17	8	0	3.114184	-0.210355	0.302853
18	8	0	1.553851	1.412397	0.042062
19	1	0	3.638136	0.554241	0.573344

Bu-2ttt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.170174	0.137801	-0.292508
2	1	0	-0.835894	-0.899825	-0.416188
3	6	0	-0.140232	0.895616	0.534104
4	1	0	-0.437898	1.939856	0.654374
5	1	0	-0.071452	0.467291	1.537082
6	7	0	1.190552	0.888689	-0.046332
7	1	0	1.416831	1.569592	-0.755234
8	6	0	-2.550015	0.162465	0.352880
9	1	0	-1.220537	0.573881	-1.298436
10	1	0	-2.485058	-0.259480	1.364300
11	1	0	-2.874050	1.203789	0.479473
12	6	0	-3.584997	-0.604238	-0.459483
13	1	0	-3.299538	-1.655617	-0.572934
14	1	0	-4.571770	-0.579718	0.013418
15	1	0	-3.690790	-0.183493	-1.465254
16	6	0	1.980637	-0.192994	0.048895
17	8	0	3.098280	-0.060599	-0.707794
18	8	0	1.763349	-1.181045	0.741168
19	1	0	3.631931	-0.855852	-0.586596

Bu-2ttq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.112026	-0.209234	-0.639503
2	1	0	-0.512797	-1.047792	-1.013338
3	6	0	-0.358004	0.440820	0.515447
4	1	0	-0.868781	1.338211	0.867734
5	1	0	-0.302356	-0.247870	1.362508
6	7	0	0.995973	0.831867	0.165255
7	1	0	1.145520	1.720555	-0.287360
8	6	0	-2.499427	-0.708954	-0.242606
9	1	0	-1.196457	0.510167	-1.464446
10	1	0	-2.926126	-1.264571	-1.086149
11	1	0	-2.402113	-1.433401	0.576835
12	6	0	-3.461721	0.402234	0.164596
13	1	0	-4.465318	0.008955	0.354457
14	1	0	-3.138925	0.915025	1.075593
15	1	0	-3.547970	1.157420	-0.624591
16	6	0	1.979979	-0.078367	0.088346
17	8	0	3.114709	0.456123	-0.427500
18	8	0	1.905591	-1.246501	0.452674
19	1	0	3.788314	-0.235741	-0.437098

Bu-2tqg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.841949	-0.856011	-0.274052
2	6	0	0.512147	-1.407191	0.233772
3	1	0	0.498471	-2.495199	0.117413
4	1	0	0.383830	-1.199500	1.297442
5	7	0	-0.644336	-0.865935	-0.456843
6	1	0	-0.680330	-0.953813	-1.461459
7	1	0	1.836856	-0.873779	-1.372462
8	1	0	2.623752	-1.561605	0.032612
9	6	0	2.226624	0.537501	0.222479
10	1	0	3.243103	0.749245	-0.132212
11	1	0	2.290855	0.520049	1.318463
12	6	0	1.305258	1.673127	-0.213536
13	1	0	1.110184	1.642321	-1.290732
14	1	0	0.342977	1.643685	0.302114
15	1	0	1.755478	2.645635	0.010809
16	6	0	-1.531069	-0.044673	0.120307
17	8	0	-1.581554	0.253142	1.309081
18	8	0	-2.416411	0.437274	-0.788885
19	1	0	-3.040561	1.004657	-0.319476

Bu-2tqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.446407	0.958366	-0.125639
2	6	0	-0.082053	1.493703	0.291619
3	1	0	-0.025774	2.569993	0.110167
4	1	0	0.081879	1.340004	1.359740
5	7	0	1.022640	0.864596	-0.410427
6	1	0	1.110469	1.032363	-1.401929
7	1	0	-1.596180	1.147956	-1.197161
8	1	0	-2.213214	1.543462	0.398575
9	6	0	-1.646445	-0.524934	0.164556
10	1	0	-1.475367	-0.713232	1.231860
11	1	0	-0.890623	-1.111381	-0.372295
12	6	0	-3.035883	-1.005369	-0.232802
13	1	0	-3.170444	-2.071993	-0.027322
14	1	0	-3.815521	-0.463450	0.313478
15	1	0	-3.218262	-0.850429	-1.301864
16	6	0	1.661698	-0.208205	0.085176
17	8	0	2.489364	-0.757832	-0.838673
18	8	0	1.561636	-0.649058	1.224089
19	1	0	2.941089	-1.501709	-0.421043

Bu-2tqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.564330	1.100153	0.207840
2	6	0	0.382566	1.213725	-0.750915
3	1	0	0.369290	2.206570	-1.208097
4	1	0	0.455868	0.492090	-1.565096
5	7	0	-0.896143	1.002648	-0.096899
6	1	0	-1.166910	1.653203	0.626133
7	1	0	1.440646	1.851492	0.998312
8	1	0	2.473666	1.378944	-0.340297
9	6	0	1.746081	-0.281137	0.834466
10	1	0	0.820684	-0.580445	1.343517
11	1	0	2.505144	-0.207932	1.622620
12	6	0	2.161150	-1.356437	-0.163039
13	1	0	2.330760	-2.316048	0.335593
14	1	0	1.399027	-1.521185	-0.928825
15	1	0	3.090703	-1.081869	-0.673905
16	6	0	-1.520917	-0.186456	-0.105087
17	8	0	-2.559770	-0.199536	0.768215
18	8	0	-1.245772	-1.147680	-0.813351
19	1	0	-3.000796	-1.054722	0.689831

Bu-2cgt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.540701	0.685517	-0.492080
2	1	0	1.600397	0.304986	-1.520666
3	6	0	0.098926	1.030539	-0.162760
4	1	0	0.023679	1.395377	0.866924
5	1	0	-0.256663	1.836006	-0.814467
6	7	0	-0.761985	-0.130597	-0.314860
7	1	0	-0.391052	-0.975667	-0.721675
8	6	0	2.176384	-0.314159	0.469337
9	1	0	2.116952	1.617979	-0.479393
10	1	0	2.087964	0.069264	1.494111
11	1	0	1.622974	-1.260898	0.451188
12	6	0	3.638911	-0.576875	0.136636
13	1	0	4.228799	0.344835	0.185131
14	1	0	4.089630	-1.294121	0.829503
15	1	0	3.748502	-0.982573	-0.874978
16	6	0	-2.050048	-0.098070	0.045053
17	8	0	-2.669448	-1.282301	-0.191345
18	8	0	-2.627559	0.868442	0.532392
19	1	0	-3.590470	-1.191839	0.082850

Bu-2ctg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.441760	-0.917402	-0.149895
2	1	0	1.372812	-0.984043	-1.243143
3	6	0	0.328200	-0.022133	0.367874
4	1	0	0.422024	0.103411	1.454277
5	1	0	0.388082	0.973358	-0.075055
6	7	0	-0.971037	-0.575694	0.034312
7	1	0	-1.075896	-1.577544	-0.023100
8	6	0	2.830998	-0.427548	0.252465
9	1	0	1.289736	-1.933792	0.236011
10	1	0	2.896686	-0.381032	1.347322
11	1	0	3.567873	-1.175684	-0.062353
12	6	0	3.202135	0.925977	-0.344268
13	1	0	2.566632	1.732319	0.033813
14	1	0	4.236886	1.193260	-0.108519
15	1	0	3.104812	0.915063	-1.435560
16	6	0	-2.075594	0.181670	-0.003207
17	8	0	-2.117671	1.397233	0.154413
18	8	0	-3.182214	-0.561851	-0.256864
19	1	0	-3.938310	0.038098	-0.282082

Bu-2ctt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.439695	-0.377698	-0.032964
2	1	0	1.410222	-0.847921	-1.024009
3	6	0	0.164726	0.415634	0.185473
4	1	0	0.186834	0.906250	1.166398
5	1	0	0.075763	1.205764	-0.564827
6	7	0	-0.998979	-0.446469	0.083226
7	1	0	-0.893302	-1.434163	0.259301
8	6	0	2.682846	0.494812	0.087408
9	1	0	1.492998	-1.194718	0.699121
10	1	0	2.619879	1.318315	-0.635389
11	1	0	2.704837	0.962117	1.080178
12	6	0	3.965351	-0.294005	-0.139611
13	1	0	3.981972	-0.745107	-1.137566
14	1	0	4.852324	0.340701	-0.050069
15	1	0	4.065808	-1.105928	0.588716
16	6	0	-2.236887	0.052437	-0.028675
17	8	0	-2.521277	1.240139	-0.140549
18	8	0	-3.173697	-0.929413	-0.019171
19	1	0	-4.039070	-0.512915	-0.116460

Bu-2ctt(C_s) (TS)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.485535	0.153523	-0.000000
2	1	0	-1.732930	-0.454857	0.879696
3	6	0	0.000000	0.460803	0.000000
4	1	0	0.263664	1.057571	-0.879918
5	1	0	0.263664	1.057571	0.879918
6	7	0	0.775055	-0.767402	0.000000
7	1	0	0.299857	-1.656799	0.000000
8	6	0	-2.329905	1.421526	-0.000000
9	1	0	-1.732930	-0.454857	-0.879696
10	1	0	-2.073329	2.028955	0.877249
11	1	0	-2.073329	2.028955	-0.877249
12	6	0	-3.822427	1.120206	-0.000000
13	1	0	-4.109535	0.538733	0.882688
14	1	0	-4.420408	2.036702	-0.000000
15	1	0	-4.109535	0.538733	-0.882688
16	6	0	2.112826	-0.747398	0.000000
17	8	0	2.807667	0.263654	0.000000
18	8	0	2.636310	-1.999392	0.000000
19	1	0	3.597864	-1.914952	0.000000

Bu-2ctt (C₁) (UBM)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.439695	-0.377698	-0.032964
2	1	0	1.410222	-0.847921	-1.024009
3	6	0	0.164726	0.415634	0.185473
4	1	0	0.186834	0.906250	1.166398
5	1	0	0.075763	1.205764	-0.564827
6	7	0	-0.998979	-0.446469	0.083226
7	1	0	-0.893302	-1.434163	0.259301
8	6	0	2.682846	0.494812	0.087408
9	1	0	1.492998	-1.194718	0.699121
10	1	0	2.619879	1.318315	-0.635389
11	1	0	2.704837	0.962117	1.080178
12	6	0	3.965351	-0.294005	-0.139611
13	1	0	3.981972	-0.745107	-1.137566
14	1	0	4.852324	0.340701	-0.050069
15	1	0	4.065808	-1.105928	0.588716
16	6	0	-2.236887	0.052437	-0.028675
17	8	0	-2.521277	1.240139	-0.140549
18	8	0	-3.173697	-0.929413	-0.019171
19	1	0	-4.039070	-0.512915	-0.116460

Bu-2ctq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.441760	-0.917402	-0.149895
2	1	0	-1.289736	-1.933792	0.236011
3	6	0	-0.328200	-0.022133	0.367874
4	1	0	-0.388082	0.973358	-0.075055
5	1	0	-0.422024	0.103411	1.454277
6	7	0	0.971037	-0.575694	0.034312
7	1	0	1.075896	-1.577544	-0.023100
8	6	0	-2.830998	-0.427548	0.252465
9	1	0	-1.372812	-0.984043	-1.243143
10	1	0	-3.567873	-1.175684	-0.062353
11	1	0	-2.896686	-0.381032	1.347322
12	6	0	-3.202135	0.925977	-0.344268
13	1	0	-4.236886	1.193260	-0.108519
14	1	0	-2.566632	1.732319	0.033813
15	1	0	-3.104812	0.915063	-1.435560
16	6	0	2.075594	0.181670	-0.003207
17	8	0	2.117671	1.397233	0.154413
18	8	0	3.182214	-0.561851	-0.256864
19	1	0	3.938310	0.038098	-0.282082

Bu-2cqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.540701	0.685517	-0.492080
2	6	0	-0.098926	1.030539	-0.162760
3	1	0	0.256663	1.836007	-0.814468
4	1	0	-0.023679	1.395377	0.866924
5	7	0	0.761985	-0.130597	-0.314860
6	1	0	0.391052	-0.975667	-0.721675
7	1	0	-1.600397	0.304986	-1.520666
8	1	0	-2.116952	1.617979	-0.479393
9	6	0	-2.176384	-0.314159	0.469337
10	1	0	-2.087963	0.069264	1.494112
11	1	0	-1.622974	-1.260898	0.451188
12	6	0	-3.638910	-0.576875	0.136636
13	1	0	-4.089629	-1.294121	0.829503
14	1	0	-4.228799	0.344835	0.185131
15	1	0	-3.748502	-0.982573	-0.874978
16	6	0	2.050048	-0.098070	0.045053
17	8	0	2.627559	0.868442	0.532392
18	8	0	2.669448	-1.282301	-0.191345
19	1	0	3.590470	-1.191839	0.082851

Bu-3tgg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.138443	1.053359	-0.367577
2	1	0	0.477999	1.423603	-1.159883
3	6	0	0.318930	0.829947	0.901259
4	1	0	0.970849	0.626830	1.752775
5	1	0	-0.248195	1.727873	1.152226
6	7	0	-0.604625	-0.294310	0.812647
7	1	0	-0.221483	-1.212887	0.979546
8	6	0	1.875550	-0.190986	-0.860181
9	1	0	1.144674	-0.952704	-1.160201
10	1	0	2.424867	0.068559	-1.772916
11	1	0	1.859014	1.855775	-0.162924
12	6	0	2.838843	-0.780322	0.163817
13	1	0	2.315877	-1.168029	1.044019
14	1	0	3.412352	-1.609939	-0.260990
15	1	0	3.554968	-0.028539	0.513886
16	6	0	-1.705938	-0.309763	0.036033
17	8	0	-2.344433	-1.315530	-0.255411
18	8	0	-2.075839	0.925688	-0.366850
19	1	0	-2.891336	0.834948	-0.876086

Bu-3tgt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.205854	0.737016	0.350167
2	1	0	-0.819059	0.291110	1.275021
3	6	0	-0.045561	1.302515	-0.459989
4	1	0	-0.416571	1.771827	-1.374615
5	1	0	0.478716	2.077158	0.101689
6	7	0	0.926144	0.297054	-0.871748
7	1	0	0.701656	-0.260717	-1.681603
8	6	0	-2.032144	-0.291138	-0.413457
9	1	0	-1.848280	1.573289	0.654978
10	1	0	-2.401738	0.160569	-1.343700
11	1	0	-1.390628	-1.128259	-0.715344
12	6	0	-3.201602	-0.817999	0.407162
13	1	0	-3.881922	-0.008907	0.694312
14	1	0	-3.785947	-1.558969	-0.147373
15	1	0	-2.854096	-1.295767	1.329645
16	6	0	1.807471	-0.292320	-0.040568
17	8	0	1.937407	0.365294	1.133242
18	8	0	2.461245	-1.294943	-0.308559
19	1	0	2.611787	-0.091968	1.651874

Bu-3tgq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.390802	-0.950502	-0.470692
2	1	0	-0.927769	-0.682837	-1.427947
3	6	0	-0.316975	-1.430019	0.501405
4	1	0	-0.784629	-1.805707	1.414604
5	1	0	0.241441	-2.262967	0.069104
6	7	0	0.631675	-0.406259	0.923551
7	1	0	0.353014	0.184460	1.692315
8	6	0	-2.243727	0.217679	0.035865
9	1	0	-3.223611	0.172920	-0.453914
10	1	0	-2.033255	-1.815616	-0.675720
11	1	0	-2.441495	0.087759	1.108458
12	6	0	-1.646239	1.599551	-0.221030
13	1	0	-0.709661	1.767138	0.315552
14	1	0	-1.439176	1.741538	-1.287369
15	1	0	-2.339233	2.390275	0.084796
16	6	0	1.527886	0.175474	0.103081
17	8	0	2.126943	1.218287	0.345257
18	8	0	1.735328	-0.535157	-1.026428
19	1	0	2.403639	-0.071279	-1.547147

Bu-3ttg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.112695	-0.611158	-0.610313
2	1	0	0.743758	0.186468	-1.267356
3	6	0	0.295790	-0.612245	0.676504
4	1	0	0.642513	-1.406215	1.342848
5	1	0	0.410008	0.325750	1.220048
6	7	0	-1.125119	-0.833458	0.451769
7	1	0	-1.438548	-1.782473	0.316278
8	6	0	2.609955	-0.430875	-0.368462
9	1	0	0.934203	-1.557588	-1.135332
10	1	0	2.968414	-1.224876	0.300093
11	1	0	3.138010	-0.576764	-1.318248
12	6	0	2.979284	0.932921	0.206529
13	1	0	2.571441	1.082737	1.210568
14	1	0	4.064786	1.053101	0.278349
15	1	0	2.599199	1.742564	-0.426239
16	6	0	-1.982368	0.098919	-0.001909
17	8	0	-3.130633	-0.123940	-0.372619
18	8	0	-1.457514	1.345289	0.019978
19	1	0	-2.144908	1.955335	-0.276348

Bu-3ttt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.140573	-0.172167	-0.290211
2	1	0	0.797204	0.848025	-0.501062
3	6	0	0.108486	-0.879117	0.577592
4	1	0	0.415281	-1.910301	0.768099
5	1	0	0.028536	-0.391143	1.551179
6	7	0	-1.217297	-0.936560	-0.019618
7	1	0	-1.413702	-1.682948	-0.668576
8	6	0	2.510672	-0.128917	0.375000
9	1	0	1.211710	-0.685624	-1.257665
10	1	0	2.426936	0.378295	1.345012
11	1	0	2.840761	-1.152441	0.595864
12	6	0	3.552148	0.573796	-0.485499
13	1	0	3.259511	1.608098	-0.696074
14	1	0	4.530999	0.601318	0.003419
15	1	0	3.678421	0.066910	-1.448243
16	6	0	-2.070977	0.100030	-0.093350
17	8	0	-3.109778	0.110504	-0.746408
18	8	0	-1.682878	1.149458	0.666487
19	1	0	-2.358740	1.834280	0.583551

Bu-3ttq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.084583	0.189218	0.647141
2	1	0	-0.477264	1.012823	1.039799
3	6	0	-0.334068	-0.456381	-0.512491
4	1	0	-0.859040	-1.341753	-0.874552
5	1	0	-0.267802	0.236303	-1.354610
6	7	0	1.010397	-0.888113	-0.160794
7	1	0	1.125272	-1.800322	0.252838
8	6	0	-2.461949	0.714271	0.247143
9	1	0	-1.186257	-0.541690	1.459931
10	1	0	-2.886071	1.265673	1.094703
11	1	0	-2.348511	1.447300	-0.562562
12	6	0	-3.438004	-0.377316	-0.180068
13	1	0	-4.434530	0.033205	-0.370623
14	1	0	-3.117566	-0.883170	-1.095767
15	1	0	-3.540097	-1.141202	0.598790
16	6	0	2.066501	-0.070792	-0.006322
17	8	0	3.157256	-0.408708	0.443574
18	8	0	1.817830	1.188472	-0.432589
19	1	0	2.631016	1.697502	-0.322690

Bu-3tqg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.773524	-0.845192	-0.167010
2	6	0	0.431503	-1.547448	0.012257
3	1	0	0.490128	-2.557758	-0.402128
4	1	0	0.196529	-1.656941	1.071243
5	7	0	-0.692436	-0.882540	-0.630649
6	1	0	-0.683979	-0.836863	-1.638717
7	1	0	2.006752	-0.775645	-1.237962
8	1	0	2.529001	-1.515158	0.262032
9	6	0	1.895952	0.538083	0.481757
10	1	0	2.955518	0.725557	0.693222
11	1	0	1.395310	0.529130	1.457596
12	6	0	1.374312	1.697190	-0.363796
13	1	0	1.872608	1.721430	-1.339137
14	1	0	0.299804	1.648665	-0.552750
15	1	0	1.569328	2.656899	0.125943
16	6	0	-1.507410	0.019827	-0.058143
17	8	0	-1.391867	0.066367	1.287336
18	8	0	-2.303896	0.726529	-0.670374
19	1	0	-2.025128	0.720541	1.609120

Bu-3tqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.417750	0.969728	-0.074321
2	6	0	-0.040059	1.475132	0.336714
3	1	0	0.016641	2.558654	0.204294
4	1	0	0.148214	1.275803	1.391867
5	7	0	1.043059	0.884957	-0.436979
6	1	0	1.082747	1.117021	-1.418502
7	1	0	-1.586455	1.209024	-1.133009
8	1	0	-2.167817	1.538240	0.490777
9	6	0	-1.629112	-0.522489	0.153623
10	1	0	-1.450995	-0.757611	1.210428
11	1	0	-0.884918	-1.093866	-0.414919
12	6	0	-3.027270	-0.971443	-0.250134
13	1	0	-3.172083	-2.043896	-0.086280
14	1	0	-3.795931	-0.443374	0.324519
15	1	0	-3.217006	-0.771656	-1.310403
16	6	0	1.720089	-0.233843	-0.119855
17	8	0	2.464063	-0.839299	-0.885846
18	8	0	1.537555	-0.620462	1.162859
19	1	0	2.077862	-1.407458	1.307816

Bu-3tqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.515001	-1.121236	0.185239
2	6	0	-0.326943	-1.206893	-0.768998
3	1	0	-0.310220	-2.188207	-1.250271
4	1	0	-0.397877	-0.469578	-1.567672
5	7	0	0.951526	-1.028659	-0.095933
6	1	0	1.210748	-1.729648	0.582630
7	1	0	-1.384917	-1.883757	0.963726
8	1	0	-2.418431	-1.402856	-0.371286
9	6	0	-1.717685	0.248347	0.830746
10	1	0	-0.788195	0.569694	1.318075
11	1	0	-2.452860	0.148705	1.638349
12	6	0	-2.191292	1.318393	-0.146011
13	1	0	-2.340298	2.278827	0.357616
14	1	0	-1.474258	1.485124	-0.953921
15	1	0	-3.145111	1.035981	-0.605040
16	6	0	1.619372	0.130509	0.047102
17	8	0	2.570360	0.298140	0.805166
18	8	0	1.168506	1.108607	-0.768769
19	1	0	1.719106	1.887627	-0.620324

Bu-3cgg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.653517	1.078174	-0.218873
2	1	0	1.563740	1.721695	-1.103456
3	6	0	0.286041	0.938398	0.432163
4	1	0	0.353253	0.341223	1.344249
5	1	0	-0.087071	1.925928	0.724563
6	7	0	-0.654171	0.304076	-0.480433
7	1	0	-0.410690	0.234665	-1.456600
8	6	0	2.319219	-0.242389	-0.608574
9	1	0	1.725356	-0.750741	-1.378343
10	1	0	3.280910	-0.012914	-1.082726
11	1	0	2.297470	1.616218	0.486774
12	6	0	2.545777	-1.183999	0.568226
13	1	0	1.603912	-1.539083	0.997401
14	1	0	3.114697	-2.068151	0.264564
15	1	0	3.106323	-0.689443	1.369294
16	6	0	-1.872483	-0.150191	-0.155810
17	8	0	-2.146878	0.010970	1.159945
18	8	0	-2.669813	-0.660510	-0.938072
19	1	0	-3.027598	-0.351568	1.319543

Bu-3cgt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.519525	0.670799	0.501915
2	1	0	-1.587956	0.269920	1.522213
3	6	0	-0.067937	0.976885	0.175464
4	1	0	0.013426	1.357063	-0.847606
5	1	0	0.311819	1.757864	0.842022
6	7	0	0.752766	-0.219287	0.310265
7	1	0	0.334453	-1.057275	0.683992
8	6	0	-2.190390	-0.286289	-0.478815
9	1	0	-2.065349	1.621414	0.511670
10	1	0	-2.097764	0.119682	-1.494480
11	1	0	-1.664915	-1.249008	-0.488169
12	6	0	-3.657638	-0.514744	-0.141699
13	1	0	-4.220445	0.424801	-0.161134
14	1	0	-4.134086	-1.199630	-0.849907
15	1	0	-3.772051	-0.944049	0.859562
16	6	0	2.056783	-0.303924	0.014001
17	8	0	2.751357	-1.307697	0.147961
18	8	0	2.548711	0.863812	-0.462793
19	1	0	3.485194	0.728944	-0.656559

Bu-3cgq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.689804	-0.963717	-0.546323
2	1	0	-1.669292	-0.623094	-1.590264
3	6	0	-0.261307	-1.093377	-0.032721
4	1	0	-0.262761	-1.185934	1.058774
5	1	0	0.195859	-2.004291	-0.430141
6	7	0	0.557216	0.047838	-0.425659
7	1	0	0.129911	0.806088	-0.933502
8	6	0	-2.606496	-0.065399	0.284740
9	1	0	-3.619368	-0.137237	-0.130249
10	1	0	-2.119442	-1.971120	-0.568922
11	1	0	-2.669565	-0.470631	1.303023
12	6	0	-2.196706	1.402084	0.348106
13	1	0	-1.258135	1.543762	0.890868
14	1	0	-2.067754	1.824875	-0.654947
15	1	0	-2.957844	1.999820	0.859329
16	6	0	1.834814	0.237852	-0.068983
17	8	0	2.515388	1.218093	-0.359286
18	8	0	2.318766	-0.795612	0.659321
19	1	0	3.241643	-0.601620	0.866441

Bu-3ctg

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.443819	-0.930329	-0.058586
2	1	0	1.440253	-1.151525	-1.133668
3	6	0	0.297923	0.014847	0.261967
4	1	0	0.325565	0.290446	1.323099
5	1	0	0.384872	0.938012	-0.313996
6	7	0	-0.973563	-0.615891	-0.060781
7	1	0	-1.000827	-1.618658	-0.165723
8	6	0	2.805396	-0.372979	0.349968
9	1	0	1.272547	-1.883374	0.458300
10	1	0	2.808386	-0.178862	1.430396
11	1	0	3.561624	-1.148442	0.180814
12	6	0	3.205013	0.891881	-0.402317
13	1	0	2.549314	1.735973	-0.168777
14	1	0	4.225411	1.196856	-0.150255
15	1	0	3.166069	0.734648	-1.485930
16	6	0	-2.167568	-0.005314	-0.047960
17	8	0	-2.062620	1.320185	0.204339
18	8	0	-3.246648	-0.556234	-0.246855
19	1	0	-2.951619	1.695913	0.172898

Bu-3ctt(C_s) (UBM)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.486071	0.103801	-0.000000
2	1	0	-1.733438	-0.504056	0.880060
3	6	0	0.000000	0.410517	0.000000
4	1	0	0.261296	1.005770	-0.880852
5	1	0	0.261296	1.005770	0.880852
6	7	0	0.770222	-0.824921	-0.000000
7	1	0	0.278607	-1.705235	-0.000000
8	6	0	-2.328825	1.372980	0.000000
9	1	0	-1.733438	-0.504056	-0.880060
10	1	0	-2.071165	1.980197	0.877105
11	1	0	-2.071165	1.980197	-0.877105
12	6	0	-3.821915	1.074472	0.000000
13	1	0	-4.110341	0.493893	0.882836
14	1	0	-4.417834	1.992338	0.000000
15	1	0	-4.110341	0.493893	-0.882836
16	6	0	2.108008	-0.903374	-0.000000
17	8	0	2.689089	0.319355	0.000000
18	8	0	2.758681	-1.944695	-0.000000
19	1	0	3.645627	0.188084	0.000000

Bu-3ctq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.443819	-0.930329	0.058577
2	1	0	1.272551	-1.883372	-0.458314
3	6	0	0.297922	0.014846	-0.261973
4	1	0	0.384873	0.938013	0.313987
5	1	0	0.325558	0.290442	-1.323106
6	7	0	-0.973563	-0.615891	0.060783
7	1	0	-1.000827	-1.618658	0.165728
8	6	0	2.805395	-0.372973	-0.349971
9	1	0	1.440252	-1.151531	1.133658
10	1	0	3.561624	-1.148438	-0.180829
11	1	0	2.808384	-0.178842	-1.430397
12	6	0	3.205012	0.891878	0.402329
13	1	0	4.225406	1.196862	0.150263
14	1	0	2.549306	1.735970	0.168809
15	1	0	3.166079	0.734627	1.485940
16	6	0	-2.167567	-0.005314	0.047962
17	8	0	-2.062620	1.320183	-0.204347
18	8	0	-3.246646	-0.556232	0.246866
19	1	0	-2.951619	1.695909	-0.172911

Bu-3cqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.689807	-0.963717	0.546320
2	6	0	-0.261309	-1.093380	0.032723
3	1	0	0.195852	-2.004297	0.430142
4	1	0	-0.262759	-1.185933	-1.058772
5	7	0	0.557216	0.047831	0.425669
6	1	0	0.129907	0.806085	0.933502
7	1	0	-1.669299	-0.623096	1.590262
8	1	0	-2.119449	-1.971119	0.568915
9	6	0	-2.606493	-0.065393	-0.284743
10	1	0	-3.619367	-0.137226	0.130244
11	1	0	-2.669563	-0.470624	-1.303027
12	6	0	-2.196694	1.402087	-0.348106
13	1	0	-1.258121	1.543761	-0.890867
14	1	0	-2.957828	1.999829	-0.859329
15	1	0	-2.067742	1.824875	0.654948
16	6	0	1.834813	0.237850	0.068984
17	8	0	2.515386	1.218092	0.359287
18	8	0	2.318760	-0.795609	-0.659327
19	1	0	3.241638	-0.601622	-0.866444

Bu-3cqt

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.519523	0.670796	0.501918
2	6	0	0.067938	0.976887	0.175463
3	1	0	-0.311821	1.757870	0.842013
4	1	0	-0.013426	1.357055	-0.847611
5	7	0	-0.752767	-0.219285	0.310272
6	1	0	-0.334447	-1.057277	0.683982
7	1	0	1.587945	0.269899	1.522210
8	1	0	2.065353	1.621407	0.511696
9	6	0	2.190390	-0.286279	-0.478823
10	1	0	2.097777	0.119713	-1.494481
11	1	0	1.664909	-1.248994	-0.488200
12	6	0	3.657634	-0.514749	-0.141697
13	1	0	4.134088	-1.199622	-0.849914
14	1	0	4.220448	0.424793	-0.161105
15	1	0	3.772034	-0.944077	0.859557
16	6	0	-2.056782	-0.303925	0.014002
17	8	0	-2.548711	0.863811	-0.462792
18	8	0	-2.751355	-1.307700	0.147958
19	1	0	-3.485193	0.728943	-0.656564

Bu-3cqq

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.653506	-1.078129	0.219099
2	6	0	-0.286034	-0.938465	-0.431969
3	1	0	0.087095	-1.926050	-0.724155
4	1	0	-0.353258	-0.341488	-1.344185
5	7	0	0.654168	-0.303928	0.480491
6	1	0	0.410674	-0.234282	1.456638
7	1	0	-1.563714	-1.721461	1.103817
8	1	0	-2.297448	-1.616338	-0.486433
9	6	0	-2.319241	0.242499	0.608523
10	1	0	-1.725394	0.751028	1.378187
11	1	0	-3.280926	0.013096	1.082721
12	6	0	-2.545823	1.183857	-0.568474
13	1	0	-3.114759	2.068062	-0.264995
14	1	0	-1.603969	1.538869	-0.997730
15	1	0	-3.106365	0.689121	-1.369434
16	6	0	1.872497	0.150231	0.155779
17	8	0	2.669826	0.660722	0.937932
18	8	0	2.146912	-0.011254	-1.159933
19	1	0	3.027639	0.351233	-1.319609

Chapter 2 NMR Study of CO₂ Capture by Butylamine in Aqueous Solution. Capture Efficiency and Gibbs Free Energy of the Capture Reaction as a Function of pH

2.1. Introduction

The atmospheric concentration of CO₂ has been monitored at Mauna Loa Observatory in Hawaii since 1958. This monitoring project has since expanded to incorporate monitoring sites in Alaska, American Samoa, and Antarctica, so as to monitor the global atmospheric CO₂ concentration. As of April 2020, the concentration of CO₂ in the atmosphere at the Mauna Loa site has reached 416.21 ppm and the globally-averaged surface CO₂ concentration is close to 413 ppm.^{1,2} Drastic cutbacks on CO₂ emissions are likely not sufficient to bring global climate change under control.³⁻⁵ Thus, there is a need for the development of negative emissions technology, and a large part of the overall CO₂ extraction will be from the capture of carbon dioxide from ambient air.⁶ However, current negative emissions technologies will not be sufficient nor economically viable.⁷⁻¹¹ The kinetics of amine-based CO₂ capture has been well studied¹²⁻¹⁶ and aqueous amines are currently used for capturing CO₂ at concentrated sources. Kortunov et al.¹⁷ recently reported a thorough investigation of the capture of CO₂ by several aqueous amines, with varying p*K*_a values, by ¹³C NMR and included time-dependence and equilibrium distribution information. They suggested that, although the solution uptake of CO₂ per load cycle is greater for stronger bases, a weak base capture system could theoretically capture more efficiently by utilizing more load cycles. The efficiency is two-fold in that the facile release reaction takes less energy to remove the CO₂ and the lower temperatures will cause far less degradation of the starting materials than current capture systems.

We have been interested in developing rubisco-based biomimetic systems for reversible CO₂ capture from ambient air.¹⁸⁻²⁰ Ribulose-1,5-bisphosphate carboxylase/oxygenase (rubisco) is the enzyme responsible for most of the carbon fixation of CO₂ from air.²¹ The active site of rubisco contains the amine group of the side chain of Lys(201) and a hydrated magnesium ion that is held in place by the carboxylic acid groups of Asp(203) and Glu(204).²² In order to accomplish its enzymatic activity, the amine group of the lysine must be carbamylated.^{23,24} This carbamylation does not require the entire enzyme, and may proceed with just the active site, the tetrapeptide KDDE. Further, recent work in our group suggests that this tetrapeptide may be able to reversibly capture CO₂ in ambient air conditions.^{18,19}

As an initial investigation, we analyzed the capture of CO₂ by aqueous butylamine, a much simplified model of the lysine side chain, (Scheme 2-1) with ¹H and ¹³C NMR techniques. In aqueous solution, the rate of the capture reaction is highly dependent on pH.

Scheme 2-1. Pathway of CO₂ Addition to Butylamine

Figure 2-1 shows the fractions of the capture system species as a function of pH. The CO₂ fraction ($f(\text{CO}_2) = [\text{CO}_2]/[\text{HCO}_3^-]$, green, using $\text{p}K_a = 6.352^{25,26}$), the butylamine fraction ($f(\text{BuNH}_2) = [\text{BuNH}_2]/[\text{BuNH}_3^+]$, red, using $\text{p}K_a = 10.6^{27}$), and the carbamate fraction ($f(\text{BuNHCOO}^-) = [\text{BuNHCOO}^-]/[\text{BuNHCOOH}]$, blue, using $\text{p}K_a = 5.74^{28}$).

Figure 2-1. Fractions of the capture system species as a function of pH. Green: CO₂ fraction (using $\text{p}K_a = 6.352$).^{25,26} Red: Amine fraction (using $\text{p}K_a = 10.6$).²⁷ Blue: Carbamate fraction (using $\text{p}K_a = 5.8$).²⁸

The primary concern is that, to capture CO₂, the amine must be present as a nucleophile and not as an ammonium group. However, at pH values where the amine is ready for capture, most of the CO₂ in solution exists as bicarbonate. Therefore, we studied the effect of pH on the butylamine capture system in the range 7.82 - 11.25 (yellow highlight in Fig. 1). Here, we report the chemical shifts and relative intensities of butylamine and its carbamic acid for a range of pH values. From these data, we determine the capture efficiency and derive the Gibbs free energy of the capture reaction as a function of solution pH.

2.2. Experimental Methods

2.2.1. Sample Preparation: pH Profile of Aqueous Butylamine

The introduction of CO₂ to the aqueous amine solution alters the pH of solution quite significantly. In this study, we introduce HCO₃⁻ to the system and we rely on the bicarbonate-carbon dioxide equilibrium to generate CO₂ that is available for capture. The two equilibria of primary interest in this study are the CO₂ addition to the amine and the bicarbonate-carbon dioxide equilibrium. It is well known that the addition of CO₂ to the amine is rapid (carbamate equilibrium) and that the hydration of CO₂ is much slower (bicarbonate equilibrium).¹⁶ Therefore, for all quantitative analyses and thermochemical determinations, including the ΔG^0 values, we waited at least 48 hours before acquiring the NMR data.

The butylamine solution was prepared in a bulk and then the pH was adjusted individually. For the bulk solution, 0.90 mL (9.1 mmol) of butylamine was added to 199.10 mL of 90% H₂O : 10% D₂O mixture. 1.15 g (13.7 mmol) of sodium bicarbonate and 30.2 mg of DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) were added to the bulk solution. The pH was monitored with an

Accumet AP115 pH meter. The pH of this initial solution was 10.10. This butylamine/bicarbonate solution was then distributed into 10 small vials, each holding 20 mL and the pH was adjusted in each individual vial using small aliquots of 3M H₂SO₄ or 1M NaOH such that the added volume of acid/base did not have a significant effect on the butylamine concentration. These samples were allowed to equilibrate without venting at room temperature for > 48 hours; the pH was monitored over time and these data are given in Table 2-1. When the pH steadied with time, the NMR spectrum was recorded. The pH of each vial was measured just after the NMR measurements and this pH value is reported with the spectra.

Table 2-1. pH Measurements over the Allowed Equilibrium Time

Sample	Acid/Base Added (μL)	pH		
		Initial	Before NMR	After NMR
	3M H ₂ SO ₄			
1	0	10.11	9.95	9.97
2	25	9.89	9.81	9.81
3	50	9.58	9.62	9.61
4	75	9.14	9.38	9.39
5	100	8.53	8.68	8.70
6	150	7.38	7.57	7.82
	1M NaOH			
7	50	10.30	10.27	10.28
8	150	10.65	10.66	10.67
9	200	10.88	10.90	10.90
10	275	11.28	11.26	11.25

2.2.2. NMR Measurements with Water Suppression

Spectra were recorded on a 600 MHz Bruker Avance III spectrometer. Water suppression was accomplished using the standard Bruker pulse program “zgpgpr” which also uses presaturation to attenuate the water signal.²⁹ The transmitter frequency offset was assigned the value of 4.696 ppm, as determined by the chemical shift of the water peak in a preliminary measurement without

presaturation. To further minimize the water signal, small sample volumes were used in the NMR tube < 0.5 mL to mitigate diffusion effects.

2.3. Results and Discussion

2.3.1. ^1H - and ^{13}C -NMR Spectra of Butylamine in Aqueous Solution

The atom numbering is defined in Scheme 2-1. Figure 2-2 shows the ^1H NMR spectrum of butylamine in aqueous solution and peaks occur at 2.61 ppm (α), 1.40 ppm (β), 1.30 ppm (γ), and 0.88 ppm (δ) and a residual water peak appears at 4.7 ppm. These peaks closely agree with the respective spectra measured in CDCl_3 solution.³⁰ The bottom of Figure 2-2 shows the ^{13}C NMR spectrum of the same sample with peaks at 43.09 ppm (α), 36.43 ppm (β), 22.08 ppm (γ) and 15.89 ppm (δ). Again, these peaks closely agree with the respective spectra measured in CDCl_3 solution.³⁰

Figure 2-2. Top: Measured ^1H NMR spectrum of butylamine in 90% H_2O : 10% D_2O solution with shifts at 2.61 ppm (α), 1.40 ppm (β), 1.30 ppm (γ), and 0.88 ppm (δ). Bottom: Measured ^{13}C NMR spectrum of butylamine in 90% H_2O : 10% D_2O solution with peaks at 43.09 ppm (α), 36.43 ppm (β), 22.08 ppm (γ), and 15.89 ppm (δ).

2.3.2. pH Profile of Species in the Capture Reaction

Table 2-2 gives the chemical shifts, multiplicity, and coupling constants for the observed signals of the ^1H spectra recorded at the ten pH values studied in the range $7.82 \leq \text{pH} \leq 11.25$. At high pH, we report signals for both the parent and the daughter species. As pH decreased, the intensities of the daughter peaks were diminished and could not be distinguished from noise at pH values ≤ 8.70 . Note that there are relatively large jumps in the pH measurements from 9.39 to 8.70 and from 8.70 to 7.82. This is because carbonate has a very poor buffering capacity in that region, and small aliquots of acid affected the pH drastically.

Table 2-2. pH Profile (zgpgpr) of Butylamine in 90% H₂O : 10% D₂O solution with added NaHCO₃ – ¹H NMR spectra

Assignment	pH														
	11.25			10.90			10.67			10.28			9.97		
	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J
Parent															
α	2.71	t	7.23	2.78	t	7.29	2.84	t	7.38	2.91	t	7.44	2.94	t	7.50
β	1.46	p	7.38	1.50	p	7.44	1.54	p	7.47	1.58	p	7.47	1.59	p	7.53
γ	1.32	sx	7.47	1.32	sx	7.50	1.35	sx	7.48	1.36	sx	7.54	1.37	sx	7.50
δ	0.89	t	7.38	0.89	t	7.41	0.90	t	7.35	0.91	t	7.41	0.91	t	7.41
Daughter															
α	2.99	q	6.64 ^{b,c}	2.99	q	6.64	2.99	q	6.62	2.99	q	6.62	2.99	q	6.62
β	1.40	m	7.36	1.41	m	7.25	1.41	m	7.26	1.41	m	7.15	1.43	m	7.11
γ							1.30	m	7.47	1.31	m	7.36	1.30	m	7.44
δ				0.88	t	7.29	0.88	t	7.35	0.88	t	7.35	0.88	t	7.38

Assignment	pH														
	9.81			9.61			9.39			8.70			7.82		
	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J	δ	Mult.	J
Parent															
α	2.95	t	7.53	2.97	t	7.53	2.97	t	7.53	2.99	t	7.53	2.99	t	7.56
β	1.60	p	7.55	1.61	p	7.56	1.62	p	7.56	1.62	p	7.58	1.62	p	7.56
γ	1.37	sx	7.50	1.37	sx	7.53	1.37	sx	7.53	1.38	sx	7.37	1.38	sx	7.49
δ	0.91	t	7.41	0.91	t	7.41	0.91	t	7.41	0.92	t	7.38	0.92	t	7.41
Daughter															
α	2.99	q	6.51	2.99	q	6.60	u.p.			u.p.					
β	u.p.			u.p.			u.p.			u.p.					
γ	1.30	m	7.40	1.30	m	7.39	1.30	m	7.48	1.30	m	7.65			
δ	0.88	t	7.38	0.88	t	7.35	0.88	t	7.35	0.87	t	6.39			

All peaks reported relative to internal standard DSS signal. δ in ppm, *J* in Hz.

^a u.p.= under parent peak.

^b A quartet is observed because $^3J_{\text{HCCH}} \approx ^3J_{\text{HNCH}}$ and the NH proton is not labile and does not undergo fast exchange with solvent, therefore the n+1 rule approximately holds.

^cThe average computed coupling constants $^3J_{\text{HNCH}} = 6.20$ Hz and $^3J_{\text{HCCH}} = 7.24$ Hz were calculated with NMR=GIAO at APFD/6-311G* SCRF=(SMD,water).

Figure 2-3 shows the NMR spectra obtained over the entire pH range studied. Spectra were scaled such that the highest peak is roughly the same intensity in each spectrum. Thus, the difference in absolute intensity of peaks in different spectra is meaningless, but the relative intensity of the daughter peaks to their respective parent peaks within a spectrum is meaningful (*vide infra*). The relative intensities of the daughter peaks go through a maximum at pH = 10.28.

Figure 2-3. Measured ^1H NMR pH profile using the water suppression technique “zgpgpr” for butylamine in 90% H_2O : 10% D_2O solution with added NaHCO_3 .

The chemical shifts for the ^1H spectra are plotted in Figure 2-4 as a function of pH. Generally, the chemical shifts of the carbamate species remain the same over the pH range while the parent peaks shift upfield with increasing pH. At low pH, the daughter δ peak is sufficiently resolved from the δ parent peak, but the daughter α and β peaks are obscured by the α , and γ parent peaks,

respectively. At high pH, the parent α and γ peaks shift upfield enough that the signals of the α and β daughter peaks no longer obscured, but the parent δ peak begins to overlap with the daughter δ peak.

Figure 2-4. Shifts of the ^1H NMR of butylamine and butylcarbamic acid as a function of pH.

2.3.3. Determination of ΔG^0

The integrations of the ^1H signals were used to obtain quantitative information about the species fractions. Because of the overlap of different daughter and parent peaks at different pH, it was necessary to rely on integrations of different daughter:parent signal pairs to get quantitative information across the whole pH range. For example, the α parent and α daughter peak overlap in the low pH region and therefore cannot inform about the species ratio, so the δ parent and δ daughter integrations were used for low pH. The identity of which daughter:parent pairs were integrated is given for each pH in the second column of Table 2-3. In the cases where two pairs

are resolved well enough to determine species fraction information, an average of the daughter:parent fraction was determined.

From this data, the mole fraction of the daughter species was abstracted and is shown as a function of pH in Figure 2-5. The maximum fraction of the carbamate species is about 28% and occurs at pH = 10.28. This is consistent with the findings of Kortunov et al,¹⁷ for amines with similar pK_a values .

Figure 2-5. Mole fraction of the carbamate species as a function of pH of the solution.

Table 2-3. Concentrations and Thermochemistry for the Butylamine pH Study with $[\text{HCO}_3^-]_0 = 68 \text{ mM}$ and $[\text{Bu-NH}_2]_0 = 45 \text{ mM}$ ^a

pH	Integrated Peaks	$[\text{CO}_2]^b$	$[\text{CO}_2]^c$	$[\text{Bu-NH-COO}^-]$	ΔG_{RI}^b	ΔG_{RI}^c	ΔG_{RI}^d	ΔG_{RI}^e
11.25	α, β	0.0001	0.0001	7.3	-1.34	-1.57	-1.98	-2.22
10.90	α, β	0.0003	0.0002	10.3	-1.33	-1.57	-1.98	-2.21
10.67	α	0.0008	0.0005	11.8	-1.33	-1.57	-1.97	-2.21
10.28	α	0.0033	0.0022	12.6	-1.37	-1.60	-2.01	-2.24
9.97	α, δ	0.0095	0.0064	11.6	-1.43	-1.66	-2.07	-2.30
9.81	α, δ	0.0154	0.0104	10.2	-1.44	-1.67	-2.08	-2.31
9.61	δ	0.0275	0.0185	8.3	-1.45	-1.69	-2.10	-2.33
9.39	δ	0.0511	0.0344	6.1	-1.46	-1.69	-2.10	-2.34
8.70	δ	0.2920	0.1968	1.7	-1.45	-1.68	-2.09	-2.32

a) Concentrations in mM and energies in kcal/mol. No carbamate signals were observed at pH = 7.817.

b) Using $pK_2 = 6.352^{25,26}$ and $pK_3 = 5.74^{28}$

c) Using $pK_2 = 6.18^{31}$ and $pK_3 = 5.74^{28}$

d) Using $pK_2 = 6.352^{25,26}$ and $pK_3 = 6.20$.

e) Using $pK_2 = 6.18^{31}$ and $pK_3 = 6.20$.

The reaction in which we are primarily interested is the capture of CO₂ by butylamine Bu–NH₂ to give the butylcarbamic acid Bu–NH–COOH (R1).

$$K_1 = [\text{Bu–NH–COOH}]/([\text{Bu–NH}_2][\text{CO}_2]) \quad (\text{Eq.1})$$

The determination of K_1 is complicated by that fact that each species in R1 engages in pH dependent equilibria (R2 – R5).

$$K_2 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \quad (\text{Eq. 2})$$

$$K_3 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (\text{Eq.3})$$

$$K_4 = [\text{H}^+][\text{Bu–NH}_2]/[\text{Bu–NH}_3^+] \quad (\text{Eq. 4})$$

$$K_5 = [\text{H}^+][\text{Bu–NH–COO}^-]/[\text{Bu–NH–COOH}] \quad (\text{Eq. 5})$$

The hydrolysis of CO₂ is described by R2a and R2b and the latter reaction is the dominant pathway for bicarbonate formation at pH above 8.³² The intermediate carbonic acid formation need not be considered in the overall equilibria because the dissociation of the proton ($\text{p}K_a = 3.7$)²⁵ and the dehydration reactions are highly favorable for H₂CO₃. The value of $\text{p}K_2$ is

somewhat uncertain and has been determined by different groups to be 6.352^{25,26} or 6.18³¹ for the overall reaction. In this work, we report the concentrations and thermochemical parameters calculated using both values of pK_2 and show that the difference is relatively small for the pH region of interest (Table 2-3). To determine the concentrations of HCO_3^- , CO_3^{2-} , and CO_2 , the mass balance equation (Eq. 6) was employed. By substitution of the equilibrium quotients K_2 and K_3 , Eq. 6 can be simplified to Eq. 7.

$$[\text{HCO}_3^-]_0 = [\text{HCO}_3^-] + [\text{CO}_2] + [\text{CO}_3^{2-}] + [\text{Bu-NH-COOH}] + [\text{Bu-NH-COO}^-] \quad (\text{Eq. 6})$$

$$[\text{HCO}_3^-] = \frac{[\text{HCO}_3^-]_0 - [\text{Bu-NH-COOH}] - [\text{Bu-NH-COO}^-]}{1 + \frac{[\text{H}^+]}{K_2} + \frac{K_3}{[\text{H}^+]}} \quad (\text{Eq. 7})$$

The ratio of the integrations for the daughter peak to parent peak integration was determined for each individual daughter/parent pairs and the agreement for any given pH was good. The average of these integration ratios is the fraction given as “X” in Eq. 8.

$$X = \frac{[\text{Bu-NH-COOH}] + [\text{Bu-NH-COO}^-]}{[\text{Bu-NH}_2] + [\text{Bu-NH}_3^+]} \quad (\text{Eq. 8})$$

With the knowledge of the initial concentration of the amine, the mass balance equation (Eq. 9) and a rearrangement of Eq. 4, one can determine $[\text{BuNH}_2]$ via Eqs. 10 and 11 and $[\text{Bu-NH-COOH}]$ via Eq. 12.

$$[\text{Bu-NH}_2]_0 = [\text{Bu-NH}_2] + [\text{Bu-NH}_3^+] + [\text{Bu-NH-COOH}] + [\text{Bu-NH-COO}^-] \quad (\text{Eq. 9})$$

$$\frac{[\text{Bu-NH}_2]_0}{1+X} = [\text{Bu-NH}_2] + [\text{Bu-NH}_3^+] \quad (\text{Eq. 10})$$

And substituting in the definition of K_4 , can solve for the butylamine concentration.

$$[\text{Bu-NH}_2] = \frac{[\text{Bu-NH}_2]_0}{(1 + X)(1 + \frac{[\text{H}^+]}{K_4})} \quad (\text{Eq. 11})$$

Then, using the same butylamine mass balance equation and the equilibrium quotient for R4, one can solve for the concentration of butylcarbamic acid concentration.

$$[\text{Bu-NH-COOH}] = \frac{[\text{Bu-NH}_2]_0 - [\text{Bu-NH}_2] - [\text{Bu-NH}_3^+]}{(1 + \frac{K_5}{[\text{H}^+]})} \quad (\text{Eq. 12})$$

The specific value for the pK_a of butylcarbamic acid is not reported in the literature. However, the pK_a value of ammonium carbamic acid (NH_2COOH) systems has been determined to be 5.74,²⁸ and this approximation to K_5 is used in Eq. 12 to obtain $[\text{Bu-NH-COOH}]$. However, we also determined the effect of adding an alkyl substituent computationally to achieve a better estimate of K_5 and that work is explained in the following section.

With the values of $[\text{CO}_2]$, $[\text{Bu-NH-COOH}]$ and $[\text{Bu-NH}_2]$ known, K_1 can be calculated from its definition (Eq. 1). Then, using $\Delta G^0 = -RT \ln K_{eq}$, the Gibbs Free Energy for R1 was determined for each pH value (Table 2-3).

2.3.4. Calibration of the R-group effect on the pK_a of Alkylcarbamic Acid

The above ΔG calculation assumes that the pK_a of H_2NCOOH at $T = 273$ K is a good approximation for the pK_a of *butylcarbamic acid* at $T = 298$ K. To estimate the validity of this approximation, we calculated the Gibbs free energy difference between carbamic acid and methylcarbamic acid using the isodesmic reactions R6 and R7.

Reaction 8 is the difference of the two equilibria, R6 - R7, and ΔG_8 is actually a $\Delta\Delta G$ that describes the difference in stability of the alkylated and non-alkylated carbamic acids. As written, a negative ΔG_8 would suggest that the alkylated carbamic acid is more acidic.

All structures were optimized using the Gaussian16 software³³ with APFD³⁴ and 6-311G basis set.^{35,36} Various amounts of polarization functions and diffuse functions³⁷ were used as well as various solvation techniques (including SMD³⁸) to get a better estimate of the thermochemistry in solution. Frequencies were calculated for the lowest-energy minimum structures of all reactants and products. The coordinates for the optimized structures are given in the Appendix. The frequencies were also calculated at $T = 273.15$ K using the *freqchk* utility³³ in Gaussian16 because the $\text{p}K_a$ reported in the literature was for the ammonium carbamic acid at 0°C. Although the $\text{p}K_a$ is temperature dependent, the relatively small change of 25 °C will not likely have a noticeable effect. The effect of raising the temperature from 0 °C to 25 °C on the $\text{p}K_a$ for acetic acid corresponds to a difference of only about 0.03 $\text{p}K_a$ units.³⁹ Thus we will discuss the dissociation reaction thermochemistry at 273.15 K and assume that the energy values are a good estimate at 298.15 K. The reaction energies are given in Table 2-4 and were found to be dependent on the level of solvation and the basis set used.

The gas phase energies with the 6-311G* basis set show that alkylated anion is more stable by about 1.25 kcal/mol. However, by adding diffuse functions to the heavy atoms, the favorability is reversed and the non-alkylated anion is more stable by 0.69 kcal/mol. Since all of the experimental results occur in aqueous solution, we also calculated the same reaction

Table 2-4. Reaction Thermochemistry Data for the Reaction R8 Calculated at APFD with Various Basis Sets and Solvation Models

Model	Basis Set	ΔG_8 (kcal/mol)	$T \cdot \Delta S_8$ (kcal/mol)	ΔG_8 (kcal/mol)	$T \cdot \Delta S_8$ (kcal/mol)
		T=273.15		T = 298.15	
Gas Phase	6-311G*	-1.254	-0.033	-1.320	-0.040
	6-311+G*	0.686	0.007	0.619	0.002
SMD	6-311G*	0.046	0.341	-0.010	0.370
Solvation	6-311+G*	1.487	-0.303	1.504	-0.331
SMD	6-311G*	0.083	0.225	0.046	0.244
Solvation	6-311+G*	0.926	-0.092	0.934	-0.099
+ 2 Explicit Water Molecules	Partial Diffuse ^a	0.590	-0.037	0.574	-0.041

^a “Partial Diffuse” means 6-311+G* for the atoms of the alkylcarbamic acids and alkylcarbamates and 6-311G* for the atoms of the two explicit solvent molecules.

thermochemistry with an SMD solvation model. In this case, the 6-311G* basis set data show that the non-alkylated anion is more stable by 0.05 kcal/mol and adding the diffuse functions increases the favorability for the non-alkylated carbamate to 1.49 kcal/mol.

Because the reaction energies calculated with SMD were quite different from the gas phase energies, we investigated further solvation by adding two explicit water molecules to each of the reactants and products. With the explicit water molecules, the calculation with the 6-311G* basis set showed the non-alkylated anion to be more stable by 0.08 kcal/mol and by adding a diffuse functions, that favorability is increased to 0.93 kcal/mol. Adding explicit water molecules with large diffuse functions could subject the system to basis set superposition error. To mitigate the error, the structures were re-optimized at a new level where diffuse functions were included on the heavy atoms within the carbamic acid and carbamate structures but not on the oxygen atoms of the explicit solvent water molecules. With this approach, the calculated

reaction energy was 0.59 kcal/mol in favor of the non-alkylated carbamate. Thus, we considered 0.59 kcal/mol to be a reasonable estimate of the reaction energy ΔG_8 .

Therefore, by adding the Gibbs free energy of R8 to the Gibbs energy associated with the carbamic acid dissociation from the literature R7, we obtain a more accurate measure of the pK_a of alkylated carbamic acid: $\Delta G_7 + \Delta G_8 \approx \Delta G_6$. Then, pK_6 was calculated to be 6.20. Replacing ΔG_5 and K_5 with the alkyl-corrected ΔG_6 and K_6 , the calculated CO₂ capture reaction becomes even more favorable. The last two columns of Table 2-3 give the values for ΔG_1 calculated with the alkyl-corrected estimate of pK_5 .

The various ΔG values for the reaction R1 calculated in this work are plotted in Figure 2-6. The difference between the orange and blue colors designate the use of the two different values for pK_2 found in the literature for the overall carbonic acid equilibria. The solid curves are the values calculated using the estimate of $pK_5 = 5.74$, which is directly the pK_a for the carbamic acid H₂NCOOH. However, the dashed curves are our best estimate of ΔG_{R1} because we incorporate the effect of alkylation on the carbamic acid dissociation constant. The black curve denotes the ionic strength of solution and is plotted on the secondary axis. Deviations from ideal behavior from ionic strength effects were not considered in the calculations of ΔG and this could explain some of the fluctuations within the calculated ΔG values.

Figure 2-6. Dependence of the Gibbs free energy of the capture reaction on pH of the solution. Blue: $pK_2 = 6.352$,^{25,26} Orange: $pK_2 = 6.18$,³¹ Solid: $pK_5 = 5.74$; Dashed: $pK_5 = 6.20$. The black line denotes the ionic strength of solution and is plotted on the secondary axis.

The results of the thermochemical analysis from the computational study of small alkylamines, discussed in the previous chapter, are given in Table 2-5. Taking the average of the Gibbs free energy values calculated by the best method in Table 2-3, we obtain $\Delta G_6 = -2.28$ kcal/mol. This values is in very good agreement with the value -3.03 kcal/mol for the CO₂ capture by butylamine found in the computational study.

Table 2-5. Thermochemistry^a from Computational Study for Reaction: $R-NH_2 \rightleftharpoons R-NH-COOH$

Capture System	ΔH	ΔS	ΔG	ΔA
Ethylamine	-13.10	-35.32	-2.57	-1.98
Propylamine	-13.40	-34.78	-3.03	-2.43
Butylamine	-13.27	-34.36	-3.03	-2.50

^aEnergies for ΔH , ΔG , and ΔA in kcal/mol, ΔS in cal/mol, calculated at APFD/6-311G* SCRF=(SMD,water).

2.4. Conclusion

The capture of CO₂ by butylamine was studied in aqueous solution via ¹H NMR spectroscopy. This reaction is known to be pH sensitive and we studied the capture over a wide range of pH values. The average Gibbs free energy for the CO₂ capture reaction of butylamine was determined to be $\Delta G = -2.28$ kcal/mol. This is in very good agreement with the theoretically calculated thermochemical data. To achieve a better estimate of the overall ΔG for the reaction, we required a good estimate of the equilibrium constants for the reactions involved, including the equilibrium constant for the dissociation of an alkylated carbamic acid. A study of isodesmic reactions R6, R7, and R8 yielded an estimate of the pK_a of methylcarbamic acid, which is approximately 6.20.

The overall goal of this research was to provide a benchmark for the thermochemistry of the capture of CO₂ by the lysine side chain in the tetrapeptide KDDE. The slightly exergonic nature of the capture reaction by butylamine is indicative of a very effective capture-and-release system. Further study will focus on both the capture of KDDE and developing strategies to improving the efficiency of the capture reaction.

2.5. References

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2.6. Appendix

APFD/6-311G*

Gas Phase

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.184473	-0.000000	-0.012005
2	7	0	1.288001	0.000015	-0.110221
3	1	0	1.653982	0.833343	0.333729
4	1	0	1.653979	-0.833316	0.333721
5	8	0	-0.701086	1.136024	0.011008
6	8	0	-0.701055	-1.136041	0.011008

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.041838	0.126221	-0.001047
2	7	0	1.269668	-0.216497	-0.026049
3	1	0	1.949838	0.514108	0.068933
4	1	0	1.555003	-1.172711	0.079411
5	8	0	-0.484998	1.249814	0.003240
6	8	0	-0.816619	-0.987979	0.001475
7	1	0	-1.728552	-0.677923	0.002564

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.521208	0.109189	-0.000002
2	7	0	-0.623186	-0.611819	-0.000005
3	1	0	-0.542367	-1.614168	0.000002
4	8	0	1.596290	-0.722746	0.000002
5	8	0	0.615659	1.316319	-0.000000
6	6	0	-1.921493	0.012624	0.000003
7	1	0	-1.770677	1.090945	-0.000039
8	1	0	-2.495499	-0.260479	-0.890454
9	1	0	-2.495466	-0.260418	0.890500
10	1	0	2.372432	-0.152605	0.000004

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.668807	0.066267	-0.031443
2	7	0	-0.594749	-0.647752	-0.261189
3	1	0	-0.503445	-1.591102	0.089491
4	8	0	1.650932	-0.690027	0.116012
5	8	0	0.593406	1.312441	-0.036607
6	6	0	-1.813131	0.015234	0.113068
7	1	0	-1.696571	1.062628	-0.170023
8	1	0	-2.684629	-0.404110	-0.414356
9	1	0	-2.040869	-0.001464	1.198219

Solvation: SMD

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.264345	0.000001	-0.088740
2	6	0	-0.142527	-0.000000	-0.002936
3	8	0	-0.712402	1.127811	0.007873
4	8	0	-0.712399	-1.127812	0.007873
5	1	0	1.701577	0.841428	0.256414
6	1	0	1.701579	-0.841425	0.256414

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.261493	-0.240951	-0.008153
2	6	0	-0.030720	0.115381	-0.000061
3	8	0	-0.454854	1.263759	0.000837
4	8	0	-0.844546	-0.967049	0.000520
5	1	0	1.965944	0.475604	0.022362
6	1	0	1.538682	-1.207435	0.023403
7	1	0	-1.755556	-0.647481	0.000814

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.515205	0.095104	-0.004762
2	7	0	-0.610413	-0.630663	-0.030376
3	1	0	-0.538647	-1.633236	0.033103
4	8	0	1.620232	-0.691480	0.009334
5	8	0	0.569896	1.320099	-0.002423
6	6	0	-1.906660	0.009282	0.012741
7	1	0	-2.011560	0.727390	-0.802657
8	1	0	-2.674291	-0.754310	-0.098472
9	1	0	-2.067929	0.532618	0.959105
10	1	0	2.393025	-0.113087	0.018389

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.823607	0.020016	0.087254
2	1	0	1.904105	0.360511	1.128623
3	1	0	1.944480	0.892311	-0.556267
4	7	0	0.573510	-0.648514	-0.205312
5	6	0	-0.635875	0.045054	-0.026386
6	8	0	-1.679292	-0.662772	0.087755
7	8	0	-0.590876	1.307916	-0.025678
8	1	0	2.652635	-0.661235	-0.113671
9	1	0	0.519153	-1.603562	0.116672

Solvation: SMD and 2 explicit water molecules

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-2.495086	0.029340	-0.147727
2	1	0	-3.010509	-0.634317	0.409212
3	1	0	-2.918974	0.941735	-0.211705
4	6	0	-1.117182	0.017090	0.028355
5	8	0	-0.488083	1.050958	-0.353339
6	8	0	-0.605371	-1.034148	0.511546
7	1	0	1.013583	-1.366178	-0.054160
8	8	0	1.939101	-1.419677	-0.371176
9	1	0	2.241558	-0.500223	-0.276779
10	1	0	1.126923	1.189919	0.000207
11	8	0	2.096749	1.270360	0.194967
12	1	0	2.176941	1.121209	1.141199

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-2.506200	-0.146806	-0.106964
2	1	0	-2.985286	-0.984392	0.176199
3	1	0	-3.043748	0.682823	-0.294528
4	6	0	-1.173297	-0.077808	0.045015
5	8	0	-0.685729	1.121042	-0.256442
6	8	0	-0.487638	-1.040336	0.411548
7	1	0	1.192558	-1.279040	0.030780
8	8	0	2.150740	-1.269918	-0.172397
9	1	0	2.218972	-1.424799	-1.119005
10	1	0	0.309680	1.171331	-0.103506
11	8	0	1.868616	1.358965	0.110700
12	1	0	1.977355	1.551580	1.046855
13	1	0	2.145732	0.418968	-0.005405

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-1.994145	0.462691	0.203684
2	1	0	-2.305376	1.388093	0.451604
3	6	0	-0.682009	0.270654	0.005114
4	8	0	0.049746	1.342149	0.305628
5	8	0	-0.215614	-0.800898	-0.407123
6	1	0	1.024345	1.194962	0.097774
7	1	0	2.651639	1.170517	-1.164837
8	1	0	2.347729	-1.652345	1.181890
9	8	0	2.576656	1.048826	-0.213502
10	1	0	2.660968	0.078355	-0.057726
11	8	0	2.306136	-1.562944	0.225295
12	1	0	1.366269	-1.382741	0.015172
13	6	0	-2.960716	-0.564435	-0.114925
14	1	0	-2.727894	-1.491693	0.411473
15	1	0	-3.944896	-0.224883	0.203111
16	1	0	-2.992814	-0.773479	-1.187753
Rotational constants (GHz):			3.9861355	1.1759060	0.9454154

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.959878	-0.452927	-0.341809
2	1	0	2.200370	-1.425045	-0.460450
3	6	0	0.610980	-0.233231	-0.120989
4	8	0	-0.173234	-1.173459	-0.465672
5	8	0	0.265431	0.879884	0.372957
6	1	0	-1.323758	1.400673	-0.142344
7	8	0	-2.255061	1.551154	-0.406246
8	1	0	-2.663199	0.692293	-0.203890
9	1	0	-1.732935	-1.100962	0.093784
10	8	0	-2.670271	-1.047130	0.416816
11	1	0	-2.601537	-0.800995	1.343532
12	6	0	2.953325	0.382526	0.296575
13	1	0	3.945144	0.072517	-0.035293
14	1	0	2.812895	1.425174	0.009033
15	1	0	2.923127	0.327463	1.391936

APFD/6-311+G*

Gas Phase

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.178383	0.000162	-0.009706
2	7	0	1.281737	-0.001181	-0.102849
3	1	0	1.673846	0.836157	0.307191
4	1	0	1.672127	-0.839380	0.307059
5	8	0	-0.701773	1.136024	0.010242
6	8	0	-0.704207	-1.134710	0.010249

Carbamic acid H2NCOOH_gas_dif.log

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.040688	0.125797	-0.000017
2	7	0	1.267638	-0.221928	-0.000165
3	1	0	1.959251	0.504831	0.000468
4	1	0	1.553872	-1.184252	0.000478
5	8	0	-0.478548	1.253414	0.000022
6	8	0	-0.822164	-0.983801	0.000016
7	1	0	-1.736769	-0.678766	0.000006

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.521464	0.109327	-0.000003
2	7	0	-0.623402	-0.608852	-0.000001
3	1	0	-0.541320	-1.612138	0.000017
4	8	0	1.596424	-0.724132	0.000001
5	8	0	0.618646	1.317728	0.000003
6	6	0	-1.924853	0.011880	-0.000001
7	1	0	-1.783113	1.091593	0.000059
8	1	0	-2.495885	-0.265445	-0.890710
9	1	0	-2.495933	-0.265534	0.890650
10	1	0	2.379844	-0.162525	-0.000011

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.818557	0.014499	0.108548
2	1	0	1.993630	0.095565	1.198328
3	1	0	1.780712	1.032068	-0.282732
4	7	0	0.589896	-0.643661	-0.248919
5	6	0	-0.665513	0.064266	-0.030119
6	8	0	-1.657568	-0.687228	0.110935
7	8	0	-0.593506	1.312491	-0.034950
8	1	0	2.681080	-0.502499	-0.335581
9	1	0	0.505633	-1.594199	0.083959

Solution: SMD

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.259956	0.000000	-0.078824
2	6	0	-0.134790	-0.000000	-0.001851
3	8	0	-0.715282	1.127210	0.007006
4	8	0	-0.715282	-1.127211	0.007006
5	1	0	1.716783	0.846761	0.225390
6	1	0	1.716783	-0.846760	0.225390

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.260261	-0.246707	0.000009
2	6	0	-0.029046	0.112953	-0.000014
3	8	0	-0.447932	1.267264	0.000004
4	8	0	-0.850559	-0.961687	-0.000005
5	1	0	1.970348	0.466501	-0.000020
6	1	0	1.534326	-1.215833	0.000010
7	1	0	-1.764294	-0.646049	0.000046

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.910408	0.009398	-0.000000
2	1	0	2.045038	0.631334	0.887717
3	1	0	2.045029	0.631349	-0.887708
4	7	0	0.610842	-0.627374	0.000001
5	6	0	-0.515019	0.093328	-0.000000
6	8	0	-1.620782	-0.692437	-0.000001
7	8	0	-0.573014	1.321688	-0.000000
8	1	0	2.673523	-0.766782	-0.000011
9	1	0	0.539255	-1.632985	-0.000002
10	1	0	-2.400706	-0.121667	0.000005

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.631085	0.041637	-0.021428
2	7	0	-0.570300	-0.644345	-0.169009
3	1	0	-0.522853	-1.614334	0.105330
4	8	0	1.687881	-0.661643	0.070717
5	8	0	0.595881	1.308539	-0.019773
6	6	0	-1.833873	0.021063	0.070903
7	1	0	-1.980486	0.837848	-0.637524
8	1	0	-2.643257	-0.695961	-0.073973
9	1	0	-1.914679	0.431497	1.084830

Solvation: SMD and 2 explicit water molecules

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	2.546739	-0.114373	-0.031773
2	1	0	3.068369	0.655508	0.358058
3	1	0	2.932592	-1.029216	0.143942
4	6	0	1.167632	-0.004406	-0.012943
5	8	0	0.500434	-1.073999	-0.173471
6	8	0	0.677267	1.157304	0.119829
7	1	0	-1.037195	1.400481	-0.028732
8	8	0	-2.016279	1.471934	-0.088212
9	1	0	-2.311529	0.543954	-0.055081
10	1	0	-1.171235	-1.210297	-0.034067
11	8	0	-2.156278	-1.296373	0.017949
12	1	0	-2.355119	-1.604310	0.907186

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.984129	-0.597437	0.062949
2	6	0	0.652763	-0.254931	-0.020331
3	8	0	-0.168124	-1.203610	-0.252030
4	8	0	0.337610	0.959758	0.162576
5	1	0	2.212225	-1.509484	-0.302007
6	1	0	-1.315266	1.450590	-0.051014
7	8	0	-2.272079	1.658187	-0.146579
8	1	0	-1.821634	-1.102094	-0.012522
9	8	0	-2.806939	-1.047226	0.085011
10	1	0	-3.003208	-1.281603	0.996930
11	1	0	-2.696998	0.783746	-0.074918
12	6	0	3.025908	0.406118	0.036511
13	1	0	2.935580	1.081723	0.888756
14	1	0	3.993506	-0.092185	0.104949
15	1	0	3.011117	1.007364	-0.879720

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-2.038507	-0.489830	-0.045887
2	1	0	-2.355541	-1.445620	-0.092439
3	6	0	-0.720442	-0.262581	0.015916
4	8	0	0.002124	-1.383188	-0.024190
5	8	0	-0.235362	0.875836	0.100889
6	1	0	1.421351	1.390568	-0.061574
7	8	0	2.381271	1.559979	-0.167632
8	1	0	2.658944	2.062783	0.604361
9	1	0	0.989188	-1.207111	0.039641
10	8	0	2.593533	-1.089580	0.136104
11	1	0	2.989551	-1.527668	-0.623816
12	1	0	2.723920	-0.122402	0.006168
13	6	0	-2.998521	0.591443	-0.003916
14	1	0	-3.997693	0.167936	-0.089669
15	1	0	-2.934433	1.144802	0.935912
16	1	0	-2.844491	1.287977	-0.830745

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.995471	-0.557164	-0.187307
2	1	0	2.212041	-1.536980	-0.086794
3	6	0	0.657116	-0.245430	-0.092618
4	8	0	-0.164833	-1.214341	-0.206047
5	8	0	0.338976	0.970890	0.073088
6	1	0	-1.324362	1.448497	-0.072912
7	8	0	-2.285201	1.651267	-0.131593
8	1	0	-2.703073	0.774966	-0.042561
9	1	0	-1.817786	-1.106518	0.028421
10	8	0	-2.802782	-1.053811	0.130922
11	1	0	-2.993368	-1.284268	1.045028
12	6	0	3.019564	0.389279	0.198367
13	1	0	3.996434	-0.072700	0.051568
14	1	0	2.974850	1.284581	-0.424014
15	1	0	2.937604	0.697429	1.246958

Partial Diffuse (APFD/6-311+G*) and (APFD/6-311G*)

Carbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	2.431938	0.023526	-0.215509
2	6	0	1.094413	-0.102890	0.115892
3	8	0	0.492833	-1.147519	-0.288272
4	8	0	0.573994	0.805057	0.832535
5	1	0	2.762984	-0.531840	-0.989318
6	1	0	-0.901156	1.453071	-0.007474
7	8	0	-1.744277	1.517042	-0.490586
8	1	0	-1.180047	-1.180929	-0.013982
9	8	0	-2.159934	-1.150594	0.108387
10	1	0	-2.293027	-1.047590	1.055190
11	1	0	-2.109264	0.620302	-0.378928
12	1	0	2.829528	0.947755	-0.148788

Carbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	2.515445	-0.152418	-0.086276
2	1	0	2.985686	-1.027208	0.075499
3	1	0	3.052475	0.652794	-0.363948
4	6	0	1.182214	-0.083597	0.044889
5	8	0	0.697740	1.124341	-0.222369
6	8	0	0.485011	-1.051428	0.382969
7	1	0	-0.304698	1.176906	-0.076048
8	1	0	-2.003724	1.597554	1.005731
9	1	0	-2.272829	-1.488229	-1.079057
10	8	0	-1.847219	1.375653	0.082726
11	1	0	-2.144904	0.441776	-0.027116
12	8	0	-2.184017	-1.261075	-0.148628
13	1	0	-1.225533	-1.285015	0.041955

Methylcarbamic acid

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	2.022659	-0.467878	-0.113968
2	1	0	2.352729	-1.398766	-0.316079
3	6	0	0.702577	-0.273768	-0.000156
4	8	0	-0.011278	-1.377727	-0.219051
5	8	0	0.204499	0.827584	0.280863
6	1	0	-0.999570	-1.223252	-0.063771
7	1	0	-2.675299	2.017159	0.453919
8	8	0	-2.555255	-1.091252	0.131840
9	1	0	-2.663067	-0.125381	-0.034733
10	8	0	-2.355480	1.535947	-0.315332
11	1	0	-1.403096	1.382619	-0.154471
12	6	0	2.966950	0.611405	0.075151
13	1	0	2.905115	1.022154	1.085545
14	1	0	3.971315	0.220881	-0.079284
15	1	0	2.794009	1.417479	-0.641267
16	1	0	-2.717802	-1.219977	1.071379

Methylcarbamate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-1.932557	-0.437323	-0.128421
2	1	0	-2.166728	-1.415471	-0.055096
3	6	0	-0.618122	-0.177497	-0.447224
4	8	0	0.074886	-1.141068	-0.908509
5	8	0	-0.194061	1.009878	-0.284843
6	1	0	2.859612	1.234212	-0.851282
7	8	0	2.206726	-1.270064	0.841854
8	1	0	2.471608	-0.347572	0.669637
9	8	0	2.444697	1.355605	0.007521
10	1	0	1.475660	1.250830	-0.149826
11	6	0	-2.717557	0.492249	0.654465
12	1	0	-2.816000	1.448127	0.137321
13	1	0	-3.717982	0.079490	0.789201
14	1	0	-2.285641	0.681654	1.643728
15	1	0	1.463462	-1.393335	0.223639

Chapter 3 Video Colorimetry of Single-Chromophore Systems Based on Vector Analysis in the 3D Color Space: Unexpected Hysteresis Loops in Oscillating Chemical Reactions

3.1. Introduction

Colorimetry is a technique that allows for the determination of the concentration of an analyte based on the color information of a given image. Most often, images are taken with a digital camera, and the pixel information is translated to intensities of red, green, and blue (RGB) light, on a scale that ranges from 0 to 255 for each color. The mixture of the RGB primary colors controls the overall color perceived by the user (Figure 3-1). Black is perceived when all three intensities are zero and white is perceived when all three intensity values are 255. Colorimetry

Figure 3-1. Close-up image of a modern phone screen showing RGB components of an array of pixels.

has been gathering increasing interest in recent years, especially with the development of smartphone cameras.¹⁻³ The multitude of useful applications has launched a wave of innovation within colorimetry to enhance standard analytical techniques⁴⁻⁶ and inform emerging neural-networking applications.⁷ The range of specialized applications includes the detection of

explosives,⁸ food additives,^{9,10} drugs,^{11,12} and various trace metals in aqueous solutions.^{13,14}

Exciting biomedical applications include protein detection and discrimination,¹ diagnosis of drug resistant diseases,¹⁵ and the monitoring of cell culture viability.¹⁶

Colorimetry intrinsically seeks to quantify concentration and it is desirable to have a physically meaningful, reliable *process* (i.e., the treatment of the RGB values) that is generalizable to all colorimetric studies. In practice, many different combinations of the R, G, and B intensity data have been shown empirically to have strong correlations with concentration, and different treatments have been more or less effective for different datasets.^{17,18} An excellent comparison of various RGB-derived parameters is given in Table 1 of Ref. 8 in which Choodum *et al.*⁸ explored various combinations of RGB data and many parameters showed strong correlation with concentration. Lopez-Molinero *et al.*¹³ compared some of the more popular treatments and also found concentration to strongly correlate with several RGB-derived parameters. Dong *et al.*¹⁹ and Lyra *et al.*⁵ explored a vector analysis approach, which relies on the Euclidean distance in color space between the sample and a reference. It is an appealing aspect of this approach that it has clear theoretical underpinnings. We will develop this basic approach for our purposes (*vide infra*).

The Belousov-Zhabotinsky oscillating chemical reactions (BZR) is a prototypical example of nonlinear dynamics.²⁰⁻²² The unstirred BZ reaction features intriguing wave propagations in real space which have been studied colorimetrically.²³⁻²⁵ Our group has been interested in studying mechanistic aspects of the bromine chemistry^{26,27} and measuring the kinetics of the stirred BZ reaction using video colorimetry methods.^{28,29} To determine the oxidation and reduction times using colorimetry, we employed the “Difference from Characteristic Color” (DCC) approach, a root-mean-square-deviation based analysis (*vide infra*), and we have shown this DCC approach

to work very well.^{28,29} In our previous studies, it was assumed that the DCC intensities would correlate with the concentration of the metal catalyst in solution. To test this assumption, we are examining here several case studies both with colorimetric methods and independent concentration measures. In the process, we developed a refined DCC method, the DCC_{ED} method, and we compared the performance of both DCC methods to the results obtained with an RGB vector-based analysis. The Vector Projection (VP) approach compares the measured RGB data of the sample to the color of a blank solution in RGB color space. With the VP approach we are able to determine the concentration of a single chromophore in dilute solution with high accuracy and reliability. As a proof of concept, we compared these colorimetric methods to UV-Vis data in a study of the concentration dependence of a simple dye solution and to theoretically calculated concentrations of phenolphthalein indicator over the course of a titration. With the reliability of the VP method demonstrated in this way, we applied it to successfully determine the concentration of Ce⁴⁺ in a cerium-catalyzed BZR. Colorimetry of a series of solutions with Ce⁴⁺ concentrations in the range of the BZ reaction shows the expected linear trace in 3D RGB space. The buildup of Ce(IV) during the fast oxidation phase of a BZR cycle initially follows a linear trace as expected. Surprisingly, however, this linearity does not persist for the entire oxidation phase and a different and complicated path is traced in the slow reduction phase. The hysteresis loops show shape-stability across BZR cycles and the origin and implications of this observation are discussed.

3.2. Methods

3.2.1. Instrumentation and Setup

For the color analyses, it is important to be as consistent as possible with the background and lighting features.³⁰ To this end, we used a white poster board as a background for each video/set of images. We used room lighting in conjunction with one or two photography lights to increase the overall light intensity. The white balance function of the camera was also used, and was adjusted, either automatically or manually, at the beginning of each dataset. Care was taken to place the camera at the beginning of each run in a given position such that the image of the reaction vessel was clear. The approximate distance from the camera to the beaker was 34 cm. Once the camera was placed, it was not moved for the duration of the data collection. Consistency in these aspects within any dataset is essential to obtaining good data; consistency across datasets is generally desirable, but less important.

UV spectra were recorded on an Agilent Cary 60 UV-Visible spectrophotometer with a Xenon flash lamp. The fiber optic dip probe accessory was used to collect data in real time. Scans were collected at a moderate scan rate over a small range of wavelengths in the region of absorbance.

3.2.2. Data Extraction from Video/Images

3.2.2.1. Video Recording and Image Collection

Videos and images were recorded with a Panasonic HC-V110 8.9 megapixel camera, which can capture video in three different formats, AVCHD, iFrame, and MP4. In this study, we used the maximum resolution of the camera, 1080p for video (AVCHD) and 3968x2232 for still images. The analysis includes selecting a small window of each image that contains a set number of

pixels (*vide infra*). A higher resolution also affords the option to use much larger sample windows, should that be desired. The capture rate of the camera for videos was 29 frames per second (fps). AoAo software^{31,32} was used to convert the videos into a series of still images without quality loss and during this conversion, the image rate was set to 10 images per second to reduce the number of files and therefore the analysis time. The effect of frame rate and sample window size on analysis time was studied previously.²⁸ For some kinetics applications, a higher frame rate would be desirable.

3.2.2.2. Placement and Size of Sample Window

After generating the images to be analyzed, some small window of pixels must be defined that will be used in the analysis. In this study, we use either a 50x50 pixel or a 100x100 pixel sample window. The placement of the window was dictated by several factors. In the BZ reaction vessel, we often add stirring elements and/or measurement probes to the beaker which obstruct the view of solution. Stirring effects (e.g., vortex from fast stirring) and reflections on the glassware from external lighting are also key features to avoid. Finally, in the BZR, CO₂ is produced over the course of reaction, giving rise to bubbles that can adhere to the walls of the glass. The sample window chosen should be relatively clear of bubbles, even in the later portions of the video when the most bubbles are present in solution. We define a sample window that is as far removed as possible from these elements to achieve an accurate estimate of the solution color (Figure 3-2).

Figure 3-2. Sample window selection to avoid the beaker labels, stir bar, glassware reflections, etc.

It should be noted that the choice of sample window also affects the path length through the solution. Even within a sample window, points on opposite sides of the grid have slightly different path lengths due to the cylindrical shape of the reaction vessel. To determine whether these differences would have any effect on the results, we analyzed a single dataset several times with different window placements. We found no measurable deviation in the average solution color and therefore find the effect of these small path length differences to be negligible.

3.2.2.3. Reference and Blank Solutions

The determination of concentration via any colorimetric method requires at least one reference solution of known concentration. The concentrations of samples can then be determined by extrapolation, within reasonable limits (i.e., dilute solutions). For the simple systems described here that start colorless and acquire color over time, the reference solution will be a single-component solution of the analyte. It is well known that the absorbance of a solution follows Beer's Law, that is, the absorbance is directly proportional to concentration for dilute solutions.³³

Therefore, reference solutions should be relatively lightly colored such that their concentrations are in the range of concentrations where Beer's Law holds. In the discussion of the study of the dye solution with our colorimetric methods, we will show at which concentrations Beer's Law begins to fail. Knowing this critical concentration, we can verify that the reference solution chosen falls within the range of linear proportionality.

Scheme 3-1. Hypothetical Results of the DCC Method Highlighting Key Points to Consider as the Reference Solution

One primary difference between the vector projection method and the DCC methods outlined below is the choice of reference solution (Scheme 3-1). For ideal results with the DCC methods, the reference solution will have the maximum concentration for which Beer's Law still holds. This is because the DCC methods calculate the concentration of a species based on the difference between the RGB intensities of the sample point and the reference point (*vide infra*) and the *direction* of color change from the reference is not included in the calculation. Therefore, the reference should be as deeply colored as possible within the limit of Beer's Law, such that images that deviate from the characteristic color can be assumed to be less colored and, therefore, correspond to less concentrated solutions. In Scheme 3-1, the region where Beer's

Law applies is shown in green. The point C is the critical point where the linear relationship of the DCC value to the concentration breaks down and, therefore, point C is the ideal reference point for DCC measurements. Point B can also be used effectively, especially if all of the measured samples are less concentrated than solution B. However, the choice of point D as a standard is poor and results will be *correlated* with concentration but the correlation *will not* be linear. It is often impossible to determine critical concentration before an experimental run, and therefore the most deeply-colored solution is used as the DCC reference image and a check is performed afterwards to ensure that the concentration of the reference image lies within the allowable interval.

Aside from a reference solution, the vector projection method also makes use of a blank solution. To ensure lighting conditions and other parameters are the same for the blank and the sample solutions, the blank images are usually taken immediately preceding the experimental trial. For our experiments, the blank image will contain the reaction vessel and either a water solution or a solution of the reaction mixture before any of the colored analyte is added. For example, the blank image for a BZR experiment was the mixture of the bromate, bromide, malonic acid, and sulfuric acid solutions before the Ce catalyst was added. It is preferred that the components of the blank solution be as similar to the sample matrix as possible.

3.2.3. Measurement of RGB Values

For each sample image, the RGB values are extracted via a simple Mathematica program using the built-in ImageData³⁴ function. This gives an $[m \times n \times 3]$ three-dimensional array of the red, green, and blue color values for each pixel for a given image (Figure 3-3).

Figure 3-3. Illustration of the sample window being divided into a pixel grid. This grid is analyzed such that each pixel outputs three values (R, G, and B) that are stored in a three-dimensional matrix of RGB values, shown on the right.

Then, we average over the red values, the green values, and the blue values of the pixels to get composite RGB values for each image (i) of the sample (Eq. 1-3).

$$R_{s,i} = \frac{\sum_1^m \sum_1^n R_{m,n}}{m*n} \quad (\text{Eq. 1})$$

$$G_{s,i} = \frac{\sum_1^m \sum_1^n G_{m,n}}{m*n} \quad (\text{Eq. 2})$$

$$B_{s,i} = \frac{\sum_1^m \sum_1^n B_{m,n}}{m*n} \quad (\text{Eq. 3})$$

These composite values correspond to a single point ($R_{s,i}$, $G_{s,i}$, $B_{s,i}$) in the RGB color space. The pixels in the blank and reference images are averaged in the same way to obtain the composite R_b , G_b , B_b and R_r , G_r , and B_r values, respectively.

3.2.4. DCC₀ and DCC_{ED} Methods

Conceptually, the DCC analysis measures the difference between the color of a given sample and a reference image. Therefore, the DCC analysis relies both on the (R_s , G_s , B_s) points of the

sample and the reference point (R_r , G_r , B_r). The DCC method is applied here in two ways, to determine the original DCC_0 values and a second set of DCC_{ED} values.

The equation for the determination of the originally described DCC_0 values^{28,29} is shown in Eq. 4.

$$DCC_{0,i}(R_{s,i}, G_{s,i}, B_{s,i}) = 1 - \left(\frac{R_{s,i}-R_r}{255}\right)^2 + \left(\frac{G_{s,i}-G_r}{255}\right)^2 + \left(\frac{B_{s,i}-B_r}{255}\right)^2 \quad (\text{Eq. 4})$$

The division by 255 ensures that each of the terms is less than one and the squaring ensures that each term is positive.

In the process of working on the current project, we realized that the DCC approach could be made more physically meaningful. Specifically, we define the new parameter DCC_{ED} via Eq. 5.

$$DCC_{ED,i}(R_{s,i}, G_{s,i}, B_{s,i}) = 1 - \frac{1}{\sqrt{3}} \sqrt{\left(\frac{R_{s,i}-R_r}{255}\right)^2 + \left(\frac{G_{s,i}-G_r}{255}\right)^2 + \left(\frac{B_{s,i}-B_r}{255}\right)^2} \quad (\text{Eq. 5})$$

By taking the square root of the three summed terms in Eq. 4, the new chromapostasi function DCC_{ED} now reflects the Euclidean distance in color space between the reference image and the sample image (Eq. 5). The term “chromapostasi” reflects that DCC_{ED} is a measure of the distance (Greek, apostasi) between points in color (Greek, chroma) space.

We emphasized above the importance of using a reference solution with a concentration at the upper end of the experimental range of interest. With Eqs. 4 and 5 the reason for this condition becomes clear: the DCC value will increase with increasing concentration until the concentration of the sample matches that of the reference solution. However, for samples with higher concentrations than the reference solution, whether within the Beer’s Law range or not, DCC will decrease. For the case studies presented in the following, it is always the case that the

concentrations of the DCC reference solutions exceed the concentration range of the sample solutions.

3.2.5. Vector Projection

The vector projection method relies on the difference vectors $\vec{A}$ which are defined with Eq. 6 by the difference between the sample $(R_{s,i}, G_{s,i}, B_{s,i})$ point and the blank point (R_b, G_b, B_b) . A difference vector $\vec{B}$ is defined for the reference image as shown in Eq. 7.

$$\vec{A}_i = (R_{s,i}, B_{s,i}, G_{s,i}) - (R_b, G_b, B_b) \quad (\text{Eq. 6})$$

$$\vec{B} = (R_r, B_r, G_r) - (R_b, G_b, B_b) \quad (\text{Eq. 7})$$

$$\|\vec{A}_i\| = \sqrt{(R_{s,i} - R_b)^2 + (G_{s,i} - G_b)^2 + (B_{s,i} - B_b)^2} \quad (\text{Eq. 8})$$

$$\|\vec{B}\| = \sqrt{(R_r - R_b)^2 + (G_r - G_b)^2 + (B_r - B_b)^2} \quad (\text{Eq. 9})$$

The magnitudes of vectors $\vec{A}$ and $\vec{B}$ are given by Eqs. 8 and 9, respectively. We will show that these magnitudes are directly proportional to concentration over a given range. Thus, by comparing the magnitude $\|\vec{A}_i\|$ of the i^{th} sample image to that of the reference solution $\|\vec{B}\|$, we can estimate to a very good approximation the concentration of the sample using Eq. 10.

$$[A]_i = \frac{\|\vec{A}_i\|}{\|\vec{B}\|} [B] \quad (\text{Eq. 10})$$

In an ideal Beer's Law scenario, the trace of the $\vec{A}_i$ vectors defines a straight line in color space and fall along the same line as the $\vec{B}$ vector. In reality, the $\vec{A}_i$ vectors may deviate somewhat from the direction of the $\vec{B}$ vector. In those cases, the sample vectors would need to be projected

onto the $\vec{B}$ standard vector to estimate the concentration. The vector projected magnitude (VPM) of vector $\vec{A}_i$ is provided by Eq. 11, where θ_i is the angle between each sample vector $\vec{A}_i$ and the reference vector $\vec{B}$. The angle θ_i can be determined by Eq. 12. Small θ values indicate that the vectors are directionally similar and therefore that the sample is a different shade of the same color as the reference solution.

$$\text{VPM}_i = \|\vec{A}_i\| \cos \theta_i \quad (\text{Eq. 11})$$

$$\cos \theta = \frac{\vec{A} \cdot \vec{B}}{\|\vec{A}\| \|\vec{B}\|} \quad (\text{Eq. 12})$$

The θ parameter becomes important in multi-chromophore systems. In a reaction that is accompanied by the transition from one color to another color, one would define two $\vec{B}$ vectors relative to the two reference colors. The associated $\theta_{1,i}$ and $\theta_{2,i}$ inform about the transition region.

In this work, we study single-chromophore solutions and, hence, the θ values are typically very small and not reported. Note that θ may get very large when the sample vectors have almost no magnitude and in these low-concentration cases θ merely reflects a signal:noise ratio error. Of course, when $\theta_i \approx 0$, VPM_i is approximated by $\|\vec{A}_i\|$ and for the cases reported here, we refer to VPM_i simply as the chromapostasi magnitude of the VP method.

3.3. Results and Discussion

3.3.1. Concentration of a Single Colored Dye Solute

As a proof of concept, we analyzed a series of solutions of a simple food dye. Green food dye is a mixture of FD&C Yellow 5 (tartrazine) and Blue 1 (brilliant blue FCF) dissolved in water/propylene glycol (structures in Appendix). Small aliquots of the dye solution were added to a beaker containing 750 mL of water. After the addition of each aliquot, a picture of the solution was recorded with the camera and a UV-Visible spectrum was recorded in the 620 - 635 nm region. Dye was added until the color of the solution became dark green.

Figure 3-4. Full concentration profile of green food dye in the RGB color space. Every point in the top panel corresponds to one specific concentration of the dye and each point is drawn with the color of that solution. The bottom panel shows the $R_s(c)$, $G_s(c)$, and $B_s(c)$ values with increasing concentration.

The endpoints of each sample vector (R_s , G_s , B_s) are plotted in the first panel of Figure 3-4 in the 3D RGB color space as a function of dye concentration. The bottom panel of Figure 3-4 shows the decomposition of the color space points into their $R_s(c)$, $G_s(c)$, and $B_s(c)$ values as a function of the dye concentration. Note that the blank solution has the *highest* R, G, and B values and that the addition of dye *decreases* the R_s , G_s , and B_s values until all three approach zero. The appearance of “more green” solution is the result of diminished intensity in the red and blue channels. In addition, Figure 3-4 demonstrates in a compelling fashion that the intensity changes in the three color channels are not traceable. For example, the first 54 drops of green food dye deplete entirely the intensity of red color in an almost linear fashion. The blue values also decrease relatively quickly, but not linearly, and remain non-zero over the range studied. Initially, the green values remain nearly constant and begin to decrease only after the R and B intensities are well below 20.

The UV-Vis absorbance at 630 nm was measured over the entire concentration range and the measured data are shown in Figure 3-13 (Appendix). The UV-Vis data follow Beer’s Law perfectly over the entire range of dye concentrations. To evaluate whether the video analysis can produce quantitative concentration data, we plotted the chromapostasi VPM values on the primary axis as

Figure 3-5. Comparison of the Vector Projection method (Dark Blue) and the DCC methods, DCC₀ (Dark Teal) and DCC_{ED} (Orange) to UV-Vis data.

a function of the measured absorbances over the entire range (Figure 3-5, top panel, dark blue).

In Figure 3-5, we also show the chromapostasi values DCC₀ (dark teal) and DCC_{ED} (orange) plotted on the secondary axis.

The plot in Figure 3-5 shows that the VPM chromapostasi values can reflect analyte

concentration, but it also shows that the linear relation between $\|\vec{A}_i\|$ values and absorbances for

this dataset is limited to concentrations below an absorbance of 0.14. The bottom panel shows a close-up of the region in which the chromapostasi values correlate linearly with measured absorbances.

The insights of Figure 3-4 combined with the observation of Figure 3-5 suggest that chromapostasi measurements can reflect concentration changes only if the intensities in *all* channels remain above a certain threshold. In our specific case, the R intensity becomes zero after the addition of 54 drops of dye solution and for higher dye concentrations the VP method no longer tracks concentration linearly. This observation explains why some previous studies found analyses of only one color channel to sometimes be just as effective as measuring all three color channels.⁸

The bottom panel in Figure 3-5 shows that the VPM values correlate with absorbances below 0.14 (dotted line) in a linear fashion with $R^2 > 0.98$. Further reduction of the upper absorbance limit to 0.1 results in an even better linear fit with $R^2 > 0.99$ (dashed line). All three methods show somewhat linear correlation up to a certain point, and then deviate from linearity at high concentrations. The DCC_0 and DCC_{ED} values correlate with concentration and the DCC_{ED} values are better compared to the DCC_0 data.

The above discussion has one immediate consequence, namely that the selection of a shorter path length should increase the linear range of the video analysis. To make this point, the green dye experiment was performed again measuring the UV-Vis absorbance and video data in a standard quartz cuvette (1 cm path). The top portion of Figure 3-14 (Appendix) shows the R_s , G_s , and B_s values for each concentration of dye solution measured in the cuvette, analogous to the bottom panel of Figure 3-4. Similarly, the bottom panel of Figure 3-14 shows the results of the VP analysis as a function of the UV-Vis absorbance, analogous to Figure 3-5. Figure 3-14 illustrates

in a compelling fashion that the shortened path length drastically increases the concentration range in which the video analysis produces chromapostasi data that linearly correlate with concentration. With the small path length, we find an excellent linear correlation between the UV-Vis absorbances and the video data ($R^2 = 0.9953$) for the region from 0 to 1.0 absorbance, a ten-fold increase!

3.3.2. Titration of Acetic Acid with Phenolphthalein Indicator

The study of the pH titration of acetic acid is more challenging than the study of the simple dye solutions for two reasons. First, the color change in a titration occurs rapidly in a small region of the entire pH range. Second, the concentration of the colored analyte is less clear because it exists in equilibrium with other species, and therefore, its concentration must be determined by an independent method.

Figure 3-6 shows the individual R_s , G_s , and B_s values as a function of the volume of base added. This is analogous to Figure 3-4 for the dye. The color change of phenolphthalein from colorless to pink begins around 36.9 mL of base added. Note that the *increase* of pink color is reflected by a sharp *decrease* in the green channel, the complementary color. The pink of the phenolphthalein dianion is a mixed color of red and blue with red dominating (“reddish pink”). Accordingly, we observe a faster *decrease* in the blue channel as compared to the red channel with increasing chromophore concentration. Note that none of the primary color intensities dips below 20 and all three values continue to decrease with increasing $[In^{2-}]$ for the entire course of the titration. The corresponding change in color space traces out an approximately straight line.

Figure 3-6. Composite R_s , G_s , and B_s values as a function of base added shown in the 3D color space (top) and as the individual primary color intensities (bottom). The color change of phenolphthalein starts at around 36.9 mL of base added.

In Figure 3-7, we plot the results of the colorimetric analysis as a function of volume of base added. The top panel shows the results of the VP method and the bottom panel shows the results of the DCC methods. In both panels of Figure 3-7, we show the concentrations of the colored analyte on the secondary axis. The main purpose of this study is the demonstration of video-based colorimetric analysis following species concentrations. In the case of the green dye study,

we employed UV-Vis spectroscopy and Beer's Law to obtain reliable concentration information. Here, we provide reliable concentration information about the chromophore in a different way, namely via simulation of the multi-equilibrium system as a function of pH.³⁵⁻³⁷

Figure 3-7. The top and bottom panels show the results of the vector projection method (dark blue) and the DCC₀ (dark teal) and DCC_{ED} (orange) methods, respectively, as a function of the volume of base added. In both panels, the secondary axis is employed to show the calculated concentration of the colored analyte (grey). Concentrations of the colored analyte were computed in two ways: via single-dissociation approximation $pK_a = 9.5$ (squares); via the double-dissociation $pK_{eq} = 18.55$ (triangles).

Phenolphthalein is a neutral acid, H_2In , at low pH values and the loss of two protons affords a pink dianion species, In^{2-} . The overall reaction is shown below as R1 and the equilibrium constant expression is given by Eq. 13. Of course, this reaction can be split into single proton dissociation reactions R1a and R1b with the associated equilibrium constant expressions of Eq. 14 and Eq. 15.

$$K_{\text{eq}} = [\text{H}^+]^2 [\text{In}^{2-}] / [\text{H}_2\text{In}] \quad (\text{Eq. 13})$$

$$K_{\text{a},1\text{a}} = [\text{H}^+] [\text{HIn}^-] / [\text{H}_2\text{In}] \quad (\text{Eq. 14})$$

$$K_{\text{a},1\text{b}} = [\text{H}^+] [\text{In}^{2-}] / [\text{HIn}^-] \quad (\text{Eq. 15})$$

The $\text{p}K_{\text{a}}$ that is commonly associated with phenolphthalein at standard temperature is 9.7,³⁸ which is approximately the value of $\text{p}K_{\text{a},1\text{b}}$. To use this value and to treat the equilibrium as a single proton dissociation is to assume that all of the phenolphthalein in solution exists as the mono-anion prior to the color change. This is the common approximation and we have calculated the $[\text{In}^{2-}]$ values in this manner (Figure 3-7, grey squares). However, to more accurately describe the concentration of the colored species In^{2-} , the equilibrium between H_2In and HIn^- must not be neglected. It is clear that the values of $\text{p}K_{\text{a},1\text{a}}$ and $\text{p}K_{\text{a},1\text{b}}$ are similar and the dissociations are difficult to separate from each other. Still, one spectrophotometric study

reported the values of $pK_{a,1a} = 9.05$ and $pK_{a,1b} = 9.5$.³⁹ The overall reaction, the double-dissociation given in R1, would then have a pK_{eq} of 18.55. Using the mass balance equation, Eq. 16, and the equilibrium constant expressions, the concentration of the chromophore In^{2-} can be written as Eq. 17 (Figure 3-7, grey triangles).

$$[H_2In]_0 = [H_2In] + [HIn^-] + [In^{2-}] \quad (\text{Eq. 16})$$

$$[In^{2-}] = \frac{K_{eq}[H_2In]_0}{K_{eq} + K_{a,1a}[H^+] + [H^+]^2} \quad (\text{Eq. 17})$$

The top panel of Figure 3-7 shows that the curvature and the inflection point of the vector projection data appear to be in good agreement with the chromophore concentrations calculated by both the single- and double-dissociation methods. The bottom plot in Figure 3-7 shows similar agreement for the computed DCC_0 and DCC_{ED} values. However, the double-dissociation method is clearly superior because Figure 3-8 shows that a good linear correlation of the chromapostasi values as a function of chromophore concentration can only be achieved with the double-dissociation method.

In analogy to Figure 3-5, Figure 3-8 shows the correlations between the video analysis based chromapostasi values and the calculated chromophore concentration $[In^{2-}]$. The plot range starts at the emergence of color (36.905 mL of NaOH added). For all three methods, the single dissociation approximation (squares) does not provide a satisfactory linear correlation in any range, and no linear regression line is shown. On the other hand, there is a strong linear correlation between the VPM values (dark blue, primary axis) and the calculated chromophore concentration $[In^{2-}]$ by the double dissociation method (triangles). The DCC_{ED} data (orange, secondary axis) also show very strong linear correlation with the calculated $[In^{2-}]$ and in fact, the

linear fit is slightly better than for the VP data. The DCC_0 method fares far worse and the regression line is a very poor fit of the data.

Figure 3-8. Chromapostasi values as a function of the chromophore concentration. Comparison of the vector projection method (dark blue, primary axis) and the DCC_0 (dark teal) and DCC_{ED} (orange) methods (secondary axis). Chromophore concentration computed in two ways: via single-dissociation approximation $pK_a = 9.5$ (squares); using the double-dissociation $pK_{eq} = 18.55$ (triangles). R^2 values for single dissociation approximation are 0.9701 (VP), 0.9726 (DCC_{ED}), and 0.8155 (DCC_0) and for the double-dissociation are 0.9953 (VP), 0.9959 (DCC_{ED}), and 0.9178 (DCC_0).

Our results suggest that the VP method and the DCC_{ED} method will be approximately equivalent if the trace in RGB color space closely approximates a straight line. For the phenolphthalein titration, the $R_{s,i}$, $G_{s,i}$, and $B_{s,i}$ values trace out a straight line in color space with increasing $[In^{2-}]$ (Figure 3-6). This is in sharp contrast to the case study of the green dye solution, where the trace in color space (Figure 3-4) deviated greatly from linearity. It is this linearity in RGB color space in the region of interest that allows for a judgment of the applicability of the DCC method. The best one can hope for is that the DCC reference point is at the maximum of the region of linearity and in such a case, the DCC method will yield approximately equivalent results.

3.3.3. Concentration of the Ce^{4+} Catalyst in the Belousov-Zhabotinsky Oscillating Reaction

3.3.3.1. Total Concentration of the Ce^{4+} Catalyst

Our genuine interest is with BZ oscillating reactions. In the spirit of the dye analysis, it was our intent to perform video and UV-Vis spectrometric analyses on the same system simultaneously. Another approach, in the spirit of the titration study, would involve the performance of the video analysis in conjunction with the solution of the kinetic equations governing the reaction. We thought that both approaches would provide an independent evaluation of the concentration dependence of the video analyses.

The collection of the UV-Vis data presented several obstacles for the BZ reaction. At first, we attempted to use the same fiber optic dip probe as in the dye experiment. However, CO_2 bubbles produced by the BZ reaction adhere to the surface of the probe, including the surface of the mirror, rendering unreliable readings. Because the oscillation is rapid, removing an aliquot from the bulk solution and measuring its spectrum in a standard cuvette was not feasible for real-time measurements. A flow cell attachment was also considered, but complications arising because of differences between the flow cell and the bulk solution would disrupt any comparison between the UV-Vis spectroscopic and the video analyses. Ultimately, the collection of UV-Vis measurements had to be abandoned.

The mechanism and kinetic rate constants of the BZR have been discussed in the literature for some time.^{20,21} Simulations of the kinetic equations to afford real-time concentration data have been developed with some success for the Fe-catalyzed BZ reaction,²⁸ but we have been unable to produce reliable simulations for the Ce-catalyzed reaction over a wide range of reaction

conditions using the published rate constants for the Ce^{3+} oxidation and Ce^{4+} reduction processes. Thus, we also cannot compare the results of our video analysis to theoretical concentrations of the $[\text{Ce}^{4+}]$ analyte.

Reaction systems with these kinds of complicating factors are exactly the reason why video colorimetry methods are not just desirable but an essential tool. Moreover, we did establish for a series of solutions with various Ce(IV) concentrations in the range pertinent to the BZR that the trace of the single chromophore in color space is linear (*vide infra*).

The initial concentrations of the reagents in the BZ reaction studied were: KBrO_3 74.4 mM; $\text{H}_2\text{C}(\text{COOH})_2$ 100.5 mM; KBr 19.2 mM; H_2SO_4 0.882 M; $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_4 \cdot 2 \text{H}_2\text{O}$ 4.4 mM and the volume of solution was 300 mL.⁴⁰ The video of the BZ reaction was recorded for approximately 58 minutes or 3500 seconds. The video data was split into images at a frame rate of 10 images per second, which allows for easy conversion from the image domain to the time domain. The first few minutes of the video show the mixing of the reagents and the induction periods of the BZR. To avoid any leftover induction effects, our analysis begins a few moments before the second oscillation (at 500 sec) and continues until the end of the video, approximately 3,000 seconds later. The oscillation pattern remained steady over the entire duration of the video.

The individual R_s , G_s , and B_s values were plotted as a function of time in Figure 3-9 for the full time range. The primary change in the color space with each oscillation is a drastic drop in the intensity of the blue channel, which is expected for the increase of the yellow color of the solution with increasing Ce^{4+} concentration. Importantly, none of the color intensities drop

Figure 3-9. R_s , G_s , and B_s values for the Ce-catalyzed BZ reaction plotted individually for the full time range.

below 80 and, as we have shown, this suggests that the chromapostasi values are well within the region that allows for linear correlations with concentration.

Because of the large number of data points, both the VP and the DCC analyses benefit slightly from a smoothing treatment to reduce noise. Data was smoothed by taking a moving average of the magnitude for twenty-one points, the point at time t and its ten nearest neighbors in both directions on the t axis, for a full range of $t \pm 1$ sec.

Figure 3-10. Top: VP and DCC data for the Ce-catalyzed BZ reaction. The vector projection results (dark blue) are plotted on the primary axis and the results using the DCC₀ (dark teal) and DCC_{ED} (orange) approaches are plotted on the secondary axis. Bottom: Concentration of Ce⁴⁺ in the BZ reaction as determined by the VP analysis using a 0.6 mM Ce⁴⁺ standard solution.

The direct result of the vector projection method, the chromapostasi values, are plotted on the primary axis in the top panel of Figure 3-10 and the respective results of the DCC methods are plotted on the secondary axis. For the VP method, the blank image was chosen from a small set of images in the video which occurred after the bromine-containing species had been mixed, but before any cerium was added to the reaction mixture. It is clear that the period time of the

reaction is well established by all three methods and averages to about 182 seconds, although the oscillations do tend to speed up with time.

It is an important observation that VP magnitude drops to almost zero in each cycle, suggesting that the reduction of Ce^{4+} is virtually complete in each cycle. Some noise can be seen in many of the cycles when the VP magnitudes are near zero, but this phenomenon is of no concern because the solution is hardly colored in those places. As a consequence of the definition of the DCC values, the chromapostasi parameter related to the Ce^{4+} concentrations remains nonzero, even in the absence of Ce^{4+} . Figure 3-10 shows that the lowest DCC_0 and DCC_{ED} values are 0.484 and 0.585, respectively.

If the chromapostasi values derived from the VP method are directly proportional to $[\text{Ce}^{4+}]$, then the conversion to the concentration domain requires only one standard solution. A standard solution of Ce^{4+} (0.59 mM) was prepared by dissolving 0.111 g of $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_4 \cdot 2 \text{H}_2\text{O}$ in 300 mL of 1M sulfuric acid solution. Then, by application of Eq. 10, the Ce^{4+} concentration was determined as a function of time and is shown in the bottom panel of in Figure 3-10.

The maximum Ce^{4+} concentration reached in any cycle was approximately 0.77 mM, and hence, a maximum of 14.9% of the cerium in the solution is oxidized. This is compatible with early experimental determinations of the $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$ ratio determined by potentiometric methods.²⁰

The lack of a suitable standard in the DCC dataset makes concentration determinations impossible without reference to the VP data or some other independent method.

3.3.3.2. Tracing BZ Reaction Cycles in RGB Color Space

There was every reason to expect an essentially linear trace in RGB color space for the color associated with the variable $[\text{Ce}^{4+}]$ in the course of the BZ reaction. We did know that the respective trace for a series of Ce(IV) salt solutions was essentially linear (Figure 3-11, left). To generate the plot of Figure 3-11, a stock cerium solution (45.7 mM) was made by dissolving 0.868 g of $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_4 \cdot 2 \text{H}_2\text{O}$ in 30 mL of water. This stock solution was added in 200 μL aliquots to 300 mL of 0.88 M H_2SO_4 and a picture was taken after each addition. The green points in Figure 3-11 (left) fall within the range of the Ce^{4+} concentrations of the BZR and the purple points indicate higher cerium(IV) concentrations. As can be seen, the cerium salt series is essentially linear in color space and correlates linearly with $[\text{Ce}^{4+}]$. Therefore, we were confident that the VP method would accurately describe the total cerium(IV) concentration in the BZ reaction.

In the right panel of Figure 3-11, the smoothed color space trace is shown for a single oscillation of the BZ reaction. Much to our surprise, the color space trace of the BZR cycle was nothing like a simple line. Moreover, the reduction did not re-trace the path of the oxidation causing a well-defined hysteresis loop. Blue points indicate the oxidation phase of the cycle and red points show the reduction phase. During the oxidation phase, the $[\text{Ce}^{4+}]$ grows quickly and the growing

Figure 3-11. Each cycle of the BZ reaction features a color change from colorless (Ce^{3+}) to yellow (Ce^{4+}). On the left, the color data are plotted in color space for a series of solutions with various concentrations of a cerium(IV) salt and using false colors to indicate $[\text{Ce}^{4+}]$ within the range of the BZ reaction studied (green) and $[\text{Ce}^{4+}] > 0.72 \text{ mM}$ (purple). On the right, a similar plot is shown for the color data for one BZR cycle using false colors to indicate the reduction phase (red) and the much shorter oxidation phase (blue).

intensity of the yellow color of the solution is associated with an almost linear color space trace.

In the late stages of the oxidation and for the entire duration of the reduction phase, the trace deviates from linearity in a pronounced and intractable fashion. We argue that this feature is real. To demonstrate the reality of an unexpected feature, one needs to establish reproducibility and an oscillating reaction is the perfect system in that regard because, in a sense, every cycle is a reproduction with essentially the same initial conditions.

Figure 3-12. Hysteresis loops of the $[\text{Ce}^{4+}]$ colorimetric analysis in color space for sequential oxidation/reduction cycles of the cerium-catalyzed BZ reaction. False colors are used for different cycles; cycles 3 - 7 are displayed left-to-right and top-to-bottom. The overlay of the five cycles shows some migration of the hysteresis loop in RGB space, while maintaining shape-stability.

To demonstrate the reality of the observed hysteresis and its shape-stability, color space plots were generated for several individual periods of the BZ reaction (Figure 3-12) and the different

colors simply reflect different cycles. Two perspectives are shown of the overlay of these cycles. Note that the shift of the hysteresis loops in RGB space involves changes of comparable magnitude and comparable direction for the R, G, and B values; shifts of this type are commonly associated with minor lighting fluctuations. Most importantly, the fact that very similar shapes are traced out by all cycles indicates that the fluctuations in color space are not due to noise, but have real, chemical significance.

Typical discussions of the Ce-catalyzed Belousov-Zhabotinsky reaction merely refer to the oscillation between “Ce³⁺” and “Ce⁴⁺”, as we have done above. In reality however, both cerium ions are present as complexes in solution. Under BZR conditions, it is most likely that sulfate species occupy the coordination sphere⁴¹⁻⁴⁴ and the crystallographic record includes examples of such complexes.⁴⁵⁻⁴⁷ The color of Ce(IV) complexes is known to be sensitive to the nature of ligation and large shifts in the emitted light have been documented.⁴⁸ During the fast oxidation of the predominant Ce³⁺ species, the linearity of the RGB trace of the generated Ce⁴⁺ species suggests minimal changes in the ligation. It is only in the later stages of the oxidation phase that the initially-formed Ce⁴⁺ complexes optimize their coordination sphere and this may include some ligand exchanges/additions. Reduction of the cerium(IV) complexes requires the approach of bromomalonic acid, the reducing agent, and its integration into the primary coordination sphere. The primary product of bromomalonic acid oxidation is mesoxalic acid,^{22,49} itself a powerful tridentate ligand. Eventually, the ligand sphere of the freshly-reduced cerium ion will lose the organic ligands and return to the dominant cerium(III) sulfate complex. Even a minimalistic consideration must include at least three types of Ce⁴⁺ complexes with different ligands. Every type of cerium(IV) complex will have its characteristic color and, hence, it

should not be surprising that the color trace of this complicated reaction is not linear in RGB space. The BZ reaction clearly involves more than a single chromophore.

The RGB color space analysis provides compelling evidence for the presence of several similar chromophores. *A priori*, the chromophores will have their own slightly different colors and distinct extinction coefficients. In a strict sense, the RGB color space analysis therefore does not provide a perfect concentration measurement in this case. Nevertheless, the concentration curves shown in Figure 3-10 still provide the best possible estimate of total $[\text{Ce}^{4+}]$ content.

It was our original intent to compare the video analysis to UV-Vis absorbance measurements in order to validate the former by the latter. This approach relies on the assumption of one species being responsible for the UV-Vis absorbance. The color space analysis shows that there are several chromophores and alerts to possible limitations of the colorimetric determination of concentration. The UV-Vis measurement, on the other hand, would not have been able to provide any indication of the presence of multiple chromophores because of low resolution of the instrument.

3.4. Conclusion

We have developed a colorimetric method, the vector projection (VP) method, to determine the concentration of a single chromophore reliably from video data. It is one of the major advantages of the VP method that this analysis is conceptually intelligible and can be visualized in three-dimensional RGB color space. In particular, by mapping the changes in the primary color intensities in 3D color space, one can determine whether the results of the image analysis will correlate linearly with chromophore concentration. We have shown that the VP data will correlate linearly with chromophore concentration so long as the RGB vectors trace a straight

line in color space. Linear traces are more likely for processes associated with color changes that retain significant intensity in all primary color channels.

The VP method and the DCC methods both rely on one reference. The VP method uses a blank solution (measuring background) while the DCC methods use a relatively concentrated solution of the analyte (intense color standard). The VP method is insensitive to the precise choice of standard, while the selection of the DCC standard is non-trivial and a good choice requires prior knowledge of the system. The insights led to the definition of the improved DCC_{ED} method, which is capable of producing results that match the quality obtained by the VP method.

In two proof of concept studies, we compared the performance of the colorimetric methods to independent measurements of concentrations. UV-Vis absorption data provided the independent reference in an analysis of a series of dye solutions of variable concentration. Calculations of the chromophore concentration as a function of pH were employed for the quality assessment of the colorimetric analysis of the titration with phenolphthalein indicator. Both cases provide direct evidence that the VP method allows for the determination of accurate chromophore concentrations if the RGB vectors trace a straight line in color space. The titration experiment showcased excellent agreement between the colorimetrically-determined and the computed chromophore concentrations and demonstrated in a compelling fashion that the VP analysis is perfectly able to reliably capture fast color changes which follow a complicated kinetics.

The application of the colorimetric methods to the video-based analysis to a Ce-catalyzed BZ oscillating reaction provided an impressive demonstration of their powerful capabilities to study fast reactions with complicated kinetics. The colorimetric methods are easy to apply and their temporal resolution far exceeds that of visible spectroscopy instrumentation. The VP and the DCC methods all produce highly accurate timing information. The VP method is the method of

choice to measure single-chromophore concentrations over time and the VP method produces the best possible estimates of total Ce^{4+} content. Shape-stable hysteresis loops in RGB space reveal small but systematic color changes within a BZR cycle and especially in the course of the reduction phase. The hysteresis loops inform about mechanistic complexities that would have been impossible to obtain via standard spectroscopy. The observed hysteresis loops suggest changes in the ligation of the cerium(IV) chromophore and further studies are needed to explore the impact of ligands on the 320 nm absorption of cerium(IV) ions. The observation of hysteresis loops also demonstrates the advantage of three-color analysis as compared to the commonly used single-channel colorimetric methods. Observation of the BZ reaction using just the blue channel would be an obvious choice for single-channel colorimetry. Yet, this choice would preempt the discovery of the rich redox reaction chemistry.

3.5 References

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3.6. Appendix

Scheme 3-2. Structures of (a) Yellow 5 and (b) Blue 1.

Figure. 3-13. Correlation between the number of drops of dye added and the UV-Vis absorbance for the green food dye.

Figure 3-14. Analysis of a dye solution in a standard quartz cuvette including (top) composite R_s , G_s , and B_s values as a function of dye added and (bottom) the correlation between the VPM values and the UV-Vis absorbance for the full range (dotted line) and up to Absorbance =1.0 (dashed line).

Chapter 4 Simultaneous Determination of All Species Concentrations in Multi-Equilibria for Aqueous Solutions of Dihydrogen Phosphate Considering Debye-Hückel Theory

4.1. Introduction

Systems of polyprotic acids/bases inherently involve complex equilibria. Given the pH of an acid-base system at equilibrium, the concentration of each ionic species present in solution can be deduced via the solution of a polynomial.^{1,2} Generally, the order of the polynomial grows with the number of species in the acid-base equilibrium and the mathematical solution can become rather complex. Similar computations for a buffer system involving one or more polyprotic species are more complicated, and it is even more challenging to determine the concentration of each species when the effect of the ionic strength (I) of the solution is considered. Tessman and Ivanov developed software to calculate the pH of a given mixture by solution of the n^{th} degree, single-variable polynomial with consideration of ionic strength and the results agreed with experiment.³ Numerical methods also have since been developed for the calculation of all equilibrium species using the *Solver* tool in Microsoft Excel.^{4,5}

In previous work, we described the dynamical approach for the simultaneous solution of all species concentrations for multi-equilibria systems of mixtures of acids and their conjugate bases.^{6,7} The dynamical approach entails the numerical solution of a set of first-order ordinary differential equations (ODEs) derived from the chemical equilibria expressions. This approach offers significant advantages including the ability to easily treat complex systems and the facile incorporation of Debye-Hückel theory.⁷ Importantly, the approach maintains a straightforward

mathematical description of the multi-equilibria system, which requires only basic knowledge of mass action kinetic theory.

The present study extends the dynamical approach to include equilibrium problems with several multiply charged species. Our previous study of the pH profile of the NaOH titration of citric acid showed that the effects of ionic strength can be very large, especially for the highly charged species.⁷ It therefore seemed prudent to explore mixtures that contain a larger number of highly charged species. The buffer system comprised of citric acid (H_3Cit) and dibasic sodium phosphate (Na_2HPO_4) was selected because it is a widely employed buffer system with a well-defined pH profile over a wide range of pH values. Moreover, it allows one to study the distribution of phosphate species in aqueous solution over a wide pH range. We compare our results to the experimental data sets by McIlvaine⁸ and Sigma-Aldrich⁹ and demonstrate that the dynamical approach is a convenient, flexible, and accurate method for the calculation of all species in complex acid/base equilibria at various acidities and ionic strengths. The calculated pH profile simulates the experimental data with resounding agreement. We also report the equilibrium concentrations of the non-hydrogen species and discuss the effects of ionic strength on the equilibrium distribution. Experimentally, the concentrations of these species are seldom reported because of the inherent difficulty in their measurements. With the concentrations of these other species as a function of pH, researchers are able to quickly and easily determine the optimal pH for a desired equilibrium species distribution. From a more theoretical perspective, the computed concentrations of all species allow for a discussion of concentration quotients and their dependence on ionic strength. Moreover, the approaches described in the present paper will be useful to studies of ionic strength dependence of equilibria in general.¹⁰⁻¹³

4.2. Phosphate Recovery Efforts and H_2PO_4^- -Selective Molecular Sensors

The citric acid/phosphate buffer systems present an excellent opportunity to study the pH-dependence of phosphate concentrations in aqueous solution. Phosphates are essential nutrients for all life and often they are the limiting nutrient in soil for plant growth. Using mined phosphates to fertilize the soil is rapidly exhausting the supply of phosphate available.^{14,15} On the other hand, over-use of phosphate fertilizers and the inability to recycle them have caused eutrophication in natural waters.^{16,17} Thus, efforts have been made to recover phosphates from waste water and solid biowaste.^{14,18-20} Recovery of phosphate from aqueous solutions *via* adsorption by activated alumina,²¹ Gd complexes,²² Fe-Mn binary colloids,²³ iron oxide tailings,²⁴ crab shells,²⁵ red mud,²⁶ steel slag,²⁷ oxygen furnace slag,²⁸ and ferric sludge²⁹ has been shown to be pH dependent. A doubly beneficial reaction to sequester aluminum(III) with phosphate has also recently been shown to be pH and ionic strength dependent.³⁰

Electrochemical^{31,32} and optical^{33,34} sensors for phosphate have also been explored. It is well known that proteins selectively bind anions, including phosphates, in specific protonation states.³⁵⁻³⁷ Many of the optical sensors that have been developed are based on this protein chemistry and some examples of well characterized H_2PO_4^- receptors are illustrated in the Appendix (Figure 4-5) and these include H_2PO_4^- binding using amides and pyridines with a ferrocenoyl scaffold,³⁸ bis-ureas,³⁹ tetraamides together with pyridines,^{40,41} bis-indoles with pyridines,⁴² amides and ethers,⁴³ and sapphyrins.⁴⁴ The anion recognition studies require high-accuracy concentration measurements to determine accurate complexation constants.⁴⁵ Thus, knowledge of the equilibrium distribution of phosphate species becomes essential for the determination of these complexation constants in aqueous media.

4.3. Methods: Dynamical Approach to Equilibrium Concentrations

Debye-Hückel theory and its variants^{46,47} are the most common approach to approximate activity coefficients of ions in electrolyte solutions. To account for non-ideal dynamical behavior of ionic species in solution, the concentrations of the ionic species are replaced with activities a_i in the kinetic equations. The activity a_i of the i^{th} species S_i with absolute charge z is calculated *via* Equation 1. In principle, the units of $[S_i]$ can be any concentration unit (molal, molar) and we used molar concentrations, which are required as initial conditions in the ODEs.

$$a_i = f_z[S_i^z] \quad (1)$$

$$\log_{10}(f_z) = Az^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - b I \right) \quad (2)$$

$$I = 0.5 \sum_i z_i^2 [S_i] \quad (3)$$

The activity coefficients, f_z , were calculated using the Davies approximation⁴⁸ to Debye-Hückel theory (eq. 2). The coefficient $A = e^2 B / (2.3038 \pi \epsilon_0 \epsilon_r k T)$ where e is the electron charge, ϵ is the static dielectric constant of water, k is the Boltzmann constant, T is temperature, and $B = (2e^2 N_L / \epsilon_0 \epsilon_r k T)^{1/2}$.^{49,50} At room temperature, A has the approximate value of $0.5108 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, and B is approximately $0.3287 \times 10^8 \text{ kg}^{1/2} \text{ cm}^{-1} \text{ mol}^{-1/2}$.^{50,51,52} The Davies approximation includes the empirical parameter b with a static value for all ions. Davies' original work assigns $b = 0.2$ and this value was shown to give improved activity coefficients for large anions at low ionic strength based on conductivity measurements.⁴⁸ However, the parameter $b = 0.1$ also has been used in some studies for pH profiles.^{7,53} In this work, we report the results obtained using both $b = 0.1$ and $b = 0.2$. The ionic strength was calculated *via* equation 3. Included in eq. 3 are all the species participating in the kinetic equations and the cations contributed by the added salts. The counter-ion concentrations are constant and equal to the respective initial anion concentrations.

The Davies equation is thought to give a possible error of 3% at $I = 0.1 \text{ mol L}^{-1}$ and 10% at $I = 0.5 \text{ mol L}^{-1}$.⁵¹

For a buffer system of a triprotic acid, H_3A , and the salt of a second triprotic acid,

$(\text{M}^+)_n(\text{H}_{3-n}\text{B}^{n-})$, the system of equilibria and their equilibrium equations are as follows:

The equilibrium constants are given as K_{xy} where x denotes the identity of the acid and y is the dissociation number. For citric acid (H_3Cit , 2-hydroxypropane-1,2,3,-tricarboxylic acid) at room temperature, the $\text{p}K_a$ value of the carboxyl group attached to C2 is 3.13 and the $\text{p}K_a$ values for the second and third dissociations are 4.76 and 6.40.⁵⁴ The $\text{p}K_a$ values of phosphoric acid at room temperature are 2.16, 7.21, and 12.32.^{54,55} Note that the dynamical method can be employed at other temperatures with the consideration of the temperature-dependence of the equilibrium constants *via* the van't Hoff equation. The ionic strength dependence of the $\text{p}K_a$

values of various acids has been studied and in solutions with ionic strengths below 0.6, the changes to the above pK_a values are less than 0.3 for both citric acid and phosphoric acid.⁵⁶ The equilibria of eqs. 4 – 10 lead to the following kinetic differential equations according to general mass action kinetics:⁵⁷⁻⁵⁹

$$\begin{aligned}\frac{d[H^+]}{dt} = & k_{11f}[H_3A] - f_1^2 k_{11b}[H^+][H_2A^-] + f_1 k_{12f}[H_2A^-] - f_1 f_2 k_{12b}[H^+][HA^{2-}] \\ & + f_2 k_{13f}[HA^{2-}] - f_1 f_3 k_{13b}[H^+][A^{3-}] + k_{21f}[H_3B] - f_1^2 k_{21b}[H^+][H_2B^-] \\ & + f_1 k_{22f}[H_2B^-] - f_1 f_2 k_{22b}[H^+][HB^{2-}] + f_2 k_{23f}[HB^{2-}] - f_1 f_3 k_{23b}[H^+][B^{3-}] \\ & + k_{wf} - f_1^2 k_{wb}[H^+][OH^-]\end{aligned}\quad (11)$$

$$\frac{d[H_3A]}{dt} = f_1^2 k_{11b}[H^+][H_2A^-] - k_{11f}[H_3A] \quad (12)$$

$$\begin{aligned}\frac{d[H_2A^-]}{dt} = & f_1 f_2 k_{12b}[H^+][HA^{2-}] - f_1 k_{12f}[H_2A^-] \\ & + k_{11f}[H_3A] - f_1^2 k_{11b}[H^+][H_2A^-]\end{aligned}\quad (13)$$

$$\begin{aligned}\frac{d[HA^{2-}]}{dt} = & f_1 f_3 k_{13b}[H^+][A^{3-}] - f_2 k_{13f}[HA^{2-}] \\ & + f_1 k_{12f}[H_2A^-] - f_1 f_2 k_{12b}[H^+][HA^{2-}]\end{aligned}\quad (14)$$

$$\frac{d[A^{3-}]}{dt} = f_2 k_{13f}[HA^{2-}] - f_1 f_3 k_{13b}[H^+][A^{3-}] \quad (15)$$

$$\frac{d[H_3B]}{dt} = f_1^2 k_{21b}[H^+][H_2B^-] - k_{21f}[H_3B] \quad (16)$$

$$\begin{aligned}\frac{d[H_2B^-]}{dt} = & f_1 f_2 k_{22b}[H^+][HB^{2-}] - f_1 k_{22f}[H_2B^-] \\ & + k_{21f}[H_3B] - f_1^2 k_{21b}[H^+][H_2B^-]\end{aligned}\quad (17)$$

$$\begin{aligned}\frac{d[HB^{2-}]}{dt} = & f_1 f_3 k_{23b}[H^+][B^{3-}] - f_2 k_{23f}[HB^{2-}] \\ & + f_1 k_{22f}[H_2B^-] - f_1 f_2 k_{22b}[H^+][HB^{2-}]\end{aligned}\quad (18)$$

$$\frac{d[B^{3-}]}{dt} = f_2 k_{23f} [HB^{2-}] - f_1 f_3 k_{23b} [H^+][B^{3-}] \quad (19)$$

$$\frac{d[OH^-]}{dt} = k_{wf} - f_1^2 k_{wb} [H^+][OH^-] \quad (20)$$

The method calls for the assignment of the forward reaction rate constants (k_f), the backward reaction rate constants (k_b), and the initial concentrations. One significant advantage of the dynamical approach is that the species concentrations are all described as functions of time, which theoretically allows for the approximation of species concentrations far from equilibrium if accurate values of the forward and backward rate constants, k_f and k_b , are known.⁶⁰⁻⁶³ However, since we are primarily concerned with equilibrium, the k_f values were arbitrarily set to 10^2 for all reactions and the respective k_b values were determined by $K = k_f/k_b$. Since K_{xy} is fixed, k_{xyf} could be assigned any numerical value and the equilibrium concentration data would be unchanged because k_{xyb} is defined algebraically; varying k_{xyf} only affects the time at which equilibrium is reached. The system of ODEs was solved with the *NDSolve*⁶⁴ utility in *Mathematica*.⁶⁵ The resulting functions were evaluated for the interval $0 \leq t \leq 1$ seconds and plots of the species concentrations with respect to time were generated to ensure equilibrium had been established.

The data set by McIlvaine⁸ covers a broader pH range than the data reported by Sigma⁹ and we discuss the results for the former and report the results for the latter in the Appendix (Tables 4.6 and 4.7). For simplicity of comparison with experiment, we converted the volumes of dibasic sodium phosphate and citric acid given in the experimental work to concentrations; these appear in columns 2 and 3 of Table 4-1 in g/L. In the Appendix, Table 4-4 is a reproduction of Table 4-1 with these concentrations in mol/L, as they are used in the ODEs. The experimentally measured pH values are listed in column 4 of Table 4-1.

Table 4-1. Reported and Calculated pH values and Ionic Strength for a Series of Mixtures^a of the Buffer Solution

Mix.	[H ₃ Cit] ₀	[HPO ₄ ²⁻] ₀	Expt. ⁸	<i>f</i> = 1		<i>b</i> = 0.1		<i>b</i> = 0.2		Lit. ^b	Ionic Strength		
	[g/L]	[g/L]	pH	pH _{conc}	pH _{act}	pH _{conc}	pH _{act}	pH _{conc}	pH _{act}	pH _{act}	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	18.83	0.38	2.2	2.25	2.30	2.18	2.23	2.18	2.23	2.23	0.01	0.01	0.01
2	18.02	1.19	2.4	2.53	2.60	2.41	2.48	2.41	2.48	2.48	0.03	0.03	0.03
3	17.12	2.09	2.6	2.77	2.86	2.61	2.70	2.61	2.70	2.70	0.05	0.05	0.05
4	16.17	3.04	2.8	3.00	3.10	2.80	2.90	2.80	2.90	2.90	0.07	0.07	0.07
5	15.26	3.94	3.0	3.21	3.32	2.98	3.09	2.99	3.09	3.09	0.08	0.09	0.09
6	14.47	4.74	3.2	3.41	3.53	3.15	3.26	3.16	3.27	3.26	0.10	0.10	0.10
7	13.74	5.47	3.4	3.63	3.75	3.32	3.45	3.34	3.45	3.45	0.12	0.12	0.12
8	13.03	6.18	3.6	3.89	4.01	3.51	3.64	3.53	3.66	3.64	0.14	0.14	0.14
9	12.39	6.81	3.8	4.15	4.28	3.70	3.84	3.73	3.86	3.84	0.15	0.16	0.16
10	11.81	7.40	4.0	4.40	4.53	3.89	4.03	3.92	4.05	4.03	0.17	0.17	0.17
11	11.26	7.95	4.2	4.63	4.77	4.07	4.22	4.11	4.25	4.22	0.19	0.19	0.19
12	10.74	8.47	4.4	4.87	5.01	4.26	4.41	4.31	4.44	4.41	0.21	0.21	0.21
13	10.23	8.97	4.6	5.13	5.27	4.47	4.62	4.52	4.66	4.62	0.23	0.23	0.23
14	9.74	9.46	4.8	5.42	5.57	4.69	4.85	4.75	4.89	4.85	0.25	0.25	0.25
15	9.32	9.89	5.0	5.70	5.84	4.90	5.06	4.96	5.11	5.06	0.27	0.27	0.27
16	8.91	10.29	5.2	5.93	6.08	5.09	5.26	5.17	5.32	5.26	0.29	0.29	0.29
17	8.50	10.70	5.4	6.14	6.29	5.29	5.46	5.37	5.52	5.46	0.31	0.31	0.31
18	8.07	11.13	5.6	6.33	6.48	5.49	5.66	5.57	5.73	5.66	0.33	0.33	0.33
19	7.60	11.60	5.8	6.51	6.66	5.69	5.86	5.78	5.93	5.86	0.35	0.35	0.35
20	7.08	12.12	6.0	6.68	6.83	5.89	6.06	5.98	6.13	6.06	0.37	0.37	0.37
21	6.51	12.69	6.2	6.84	7.00	6.08	6.25	6.16	6.32	6.25	0.39	0.39	0.39
22	5.91	13.29	6.4	7.00	7.15	6.24	6.42	6.33	6.49	6.42	0.41	0.41	0.41
23	5.24	13.96	6.6	7.15	7.31	6.41	6.59	6.50	6.65	6.59	0.43	0.43	0.43
24	4.37	14.83	6.8	7.34	7.50	6.59	6.78	6.69	6.85	6.78	0.46	0.46	0.46
25	3.39	15.81	7.0	7.55	7.71	6.80	6.98	6.90	7.06	6.98	0.49	0.49	0.49
26	2.51	16.69	7.2	7.75	7.92	7.00	7.19	7.11	7.27	7.19	0.52	0.52	0.52
27	1.76	17.44	7.4	7.96	8.13	7.21	7.39	7.32	7.48	7.39	0.54	0.55	0.54
28	1.22	17.98	7.6	8.16	8.32	7.40	7.59	7.51	7.67	7.59	0.56	0.56	0.56
29	0.82	18.38	7.8	8.36	8.52	7.59	7.78	7.71	7.87	7.78	0.57	0.57	0.57
30	0.53	18.67	8.0	8.56	8.72	7.80	7.99	7.91	8.08	7.99	0.58	0.58	0.58

a) Volumes of buffer solutions given in ref. 8 were converted to concentrations (g/L). *I* reported in (mol/L)

b) Calculated using the method described in ref. 5 (see Appendix).

4.4. Results and Discussion

4.4.1. pH Calculation with Dynamical Method

Three sets of equilibrium concentrations were computed for each buffer mixture. One set corresponds to an ideal system, where the ionic strength of the solution is considered to have no effect on equilibrium concentrations (i.e., $f = 1$). The other two sets include the effects of ionic strength using activity coefficients calculated with the Davies⁴⁸ equation with $b = 0.1$ or $b = 0.2$. The ionic strengths of the equilibrium solutions were calculated for all three data sets and they appear in the last three columns of Table 4-1.

Electrometric measurements of H^+ concentrations correspond to the activity of H^+ rather than its concentration.⁶⁶ We calculated pH values using both concentrations and activities and refer to them as pH_{conc} and pH_{act} , respectively; $pH_{conc} = -\log[H^+]$ and $pH_{act} = -\log[a(H^+)]$. Therefore, six values of pH were determined for each buffer mixture and they are shown in columns 5 – 10 of Table 4-1: pH_{conc} and pH_{act} for $f = 1$, and pH_{conc} and pH_{act} values calculated using the Davies approximation with $b = 0.1$ and $b = 0.2$, respectively.

The experimental data⁸ are compared to the calculated pH values in Figure 4-1. The ratio $\log([HPO_4^{2-}]_0/[H_3Cit]_0)$ is used as the independent variable to achieve a compact axis that uses relative concentrations of HPO_4^{2-} and H_3Cit such that any mixture of these two will fit within a small plot window. As the ratio increases, the solution becomes more basic and ionic strength increases (secondary axis in Figure 4-1, black curve).

Figure 4-1. Comparison of experimental pH values (red curve, ref. 8) to pH values computed with various methods (blue and green curves). The black line shows the ionic strength of the solution and is plotted with respect to the secondary axis. Solid lines show pH values calculated with $f = 1$ and dashed lines represent pH values calculated with the Davies approximation with $b = 0.1$. Blue curves indicate pH_{act} and green curves indicate pH_{conc} . The orange lines and indicators show the deviation of between the $f = 1$, pH_{act} curve (solid, blue) and experiment for two mixtures in different regions of the pH profile. On the right, the experimental pH values are compared to pH values computed with $b = 0.1$ (dashed lines) and $b = 0.2$ (dotted lines).

Figure 4-1 (right). Close-up of the high-pH region.

Figure 4-1 illustrates that ionic strength greatly affects pH. The pH values calculated with $f = 1$ (solid curves) show large deviations from the experimental pH over the entire range of mixtures with average error of 9.1% and 11.9% for pH_{conc} and pH_{act} , respectively. Note that the deviation between the computed pH_{act} values and the experimental pH corresponds to the *vertical* distance between the two curves at a given value of $\log([\text{HPO}_4^{2-}]_0/[\text{H}_3\text{Cit}]_0)$. A first inspection of Figure 4-1 might suggest that the deviation is largest in the region $\log([\text{HPO}_4^{2-}]_0/[\text{H}_3\text{Cit}]_0) > 1$ (average

error of 9.5%). However, the largest deviations actually occur in the region $0.0 < \log([\text{HPO}_4^{2-}]_0/[\text{H}_3\text{Cit}]_0) < 0.1$ (average error of 14.7%). In fact, deviations are large even at very low ionic strengths with a 10.0% error at $I = 0.05$ M. Orange indicators were added to Figure 4-1 (left) to clearly illustrate this deviation.

The agreement between experiment and the data calculated with Debye-Hückel theory and $b = 0.1$ (dashed curves in Figure 4-1) is a magnitude better with average errors of only 2.1% and 1.1% for pH_{conc} and pH_{act} , respectively. The resounding agreement between experiment and the computed pH_{act} data gets even better with increasing I , especially in the region $x > 0$. The pH_{conc} values agree with experiment better than pH_{act} only at very low ionic strength ($I < 0.1$).

The graph on the right side of Figure 4-1 compares the experimental pH values to the pH_{conc} (green) and pH_{act} (blue) values computed with $b = 0.1$ (dashed) and $b = 0.2$ (dotted). Relative to the $b = 0.1$ values, the computed $b = 0.2$ data sets shift to higher pH at higher ionic strength. The pH_{act} values are overestimated and in slightly worse agreement than their $b = 0.1$ counterparts with 1.7% error with respect to experimental values. However, the pH_{conc} values still fall below the experimental pH curve and are in better agreement than the pH_{conc} values for $b = 0.1$ with an average error of 1.1%. The lower error of pH_{conc} values is due to the strong agreement in the region of low ionic strength. For $I < 0.25$, the $b = 0.2$ curves behave the same as $b = 0.1$ and yield very similar pH values. The ionic strength is shown for both $b = 0.1$ and $b = 0.2$, and they agree with each other for all mixtures.

4.4.2. Calculation of All Species Concentrations at Equilibrium with the Dynamical Method

A major advantage of the dynamical approach is that the equilibrium concentrations of all species in the system are obtained simultaneously. Table 4-2a shows the concentrations (in g/L) of H_3Cit , H_2Cit^- , HCit^{2-} , and Cit^{3-} (top) and Table 4-2b shows the concentrations of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} at equilibrium for each mixture. The computations require the specification of concentrations in units of mol/L and the results are given in mmol/L in Tables 4.5a and 4.5b (Appendix). Again, these values are reported for both the $f = 1$ data set and the data sets with activity considerations.

Table 4-2a. Calculated Citrate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ Cit]			[H ₂ Cit ⁻]			[HCit ²⁻]			[Cit ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	16.637	16.462	16.465	2.173	2.343	2.341	0.007	0.010	0.010	0.000	0.000	0.000
2	14.382	14.230	14.234	3.599	3.739	3.735	0.021	0.032	0.032	0.000	0.000	0.000
3	11.842	11.737	11.741	5.195	5.269	5.267	0.053	0.083	0.082	0.000	0.000	0.000
4	9.231	9.188	9.189	6.782	6.757	6.758	0.117	0.185	0.182	0.000	0.000	0.000
5	6.834	6.870	6.869	8.157	7.985	7.993	0.228	0.362	0.356	0.000	0.001	0.001
6	4.817	4.952	4.945	9.186	8.823	8.842	0.411	0.636	0.625	0.000	0.002	0.002
7	3.121	3.369	3.355	9.829	9.245	9.277	0.726	1.058	1.040	0.001	0.005	0.005
8	1.744	2.080	2.060	9.896	9.142	9.186	1.316	1.724	1.700	0.004	0.014	0.013
9	0.888	1.216	1.195	9.190	8.473	8.519	2.229	2.596	2.573	0.012	0.034	0.032
10	0.427	0.672	0.654	7.868	7.355	7.393	3.399	3.622	3.607	0.034	0.078	0.074
11	0.197	0.350	0.337	6.248	5.975	5.998	4.651	4.685	4.683	0.079	0.165	0.157
12	0.083	0.168	0.159	4.559	4.503	4.509	5.838	5.656	5.672	0.171	0.325	0.310
13	0.029	0.070	0.065	2.922	3.056	3.046	6.821	6.389	6.428	0.365	0.621	0.598
14	0.008	0.025	0.023	1.586	1.841	1.819	7.283	6.643	6.700	0.766	1.134	1.101
15	0.002	0.009	0.008	0.819	1.061	1.038	7.018	6.332	6.395	1.378	1.815	1.775
16	0.001	0.003	0.003	0.422	0.578	0.561	6.262	5.593	5.655	2.127	2.636	2.591
17	0.000	0.001	0.001	0.219	0.292	0.283	5.274	4.571	4.635	2.904	3.532	3.476
18	0.000	0.000	0.000	0.115	0.136	0.134	4.246	3.453	3.527	3.605	4.372	4.301
19	0.000	0.000	0.000	0.059	0.058	0.058	3.267	2.407	2.490	4.172	5.027	4.944
20	0.000	0.000	0.000	0.029	0.024	0.024	2.406	1.576	1.657	4.546	5.377	5.296
21	0.000	0.000	0.000	0.014	0.010	0.010	1.708	1.003	1.071	4.697	5.404	5.335
22	0.000	0.000	0.000	0.007	0.004	0.004	1.181	0.635	0.687	4.634	5.179	5.128
23	0.000	0.000	0.000	0.003	0.002	0.002	0.779	0.391	0.427	4.375	4.762	4.726
24	0.000	0.000	0.000	0.001	0.001	0.001	0.447	0.211	0.233	3.857	4.092	4.070
25	0.000	0.000	0.000	0.000	0.000	0.000	0.222	0.100	0.112	3.116	3.238	3.226
26	0.000	0.000	0.000	0.000	0.000	0.000	0.105	0.046	0.052	2.363	2.422	2.416
27	0.000	0.000	0.000	0.000	0.000	0.000	0.046	0.020	0.022	1.684	1.711	1.708
28	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.009	0.010	1.180	1.192	1.191
29	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.004	0.004	0.795	0.800	0.799
30	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.001	0.002	0.516	0.519	0.518

a) Concentrations in g/L. Data computed for the mixtures listed in Table 4-1.

Table 4-2b. Calculated Phosphate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ PO ₄]			[H ₂ PO ₄ ⁻]			[HPO ₄ ²⁻]			[PO ₄ ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	0.176	0.168	0.168	0.214	0.222	0.222	0.000	0.000	0.000	0.000	0.000	0.000
2	0.363	0.351	0.351	0.843	0.856	0.855	0.000	0.000	0.000	0.000	0.000	0.000
3	0.418	0.410	0.410	1.701	1.709	1.708	0.000	0.000	0.000	0.000	0.000	0.000
4	0.394	0.393	0.393	2.685	2.685	2.685	0.000	0.000	0.000	0.000	0.000	0.000
5	0.330	0.338	0.338	3.659	3.651	3.651	0.000	0.001	0.001	0.000	0.000	0.000
6	0.256	0.273	0.272	4.537	4.520	4.520	0.001	0.001	0.001	0.000	0.000	0.000
7	0.183	0.209	0.207	5.346	5.319	5.321	0.001	0.002	0.002	0.000	0.000	0.000
8	0.116	0.149	0.147	6.128	6.094	6.096	0.003	0.004	0.004	0.000	0.000	0.000
9	0.071	0.105	0.102	6.810	6.775	6.777	0.006	0.007	0.007	0.000	0.000	0.000
10	0.043	0.073	0.070	7.423	7.393	7.395	0.011	0.013	0.013	0.000	0.000	0.000
11	0.027	0.050	0.048	7.982	7.959	7.961	0.021	0.022	0.022	0.000	0.000	0.000
12	0.017	0.034	0.032	8.499	8.483	8.484	0.038	0.038	0.038	0.000	0.000	0.000
13	0.010	0.022	0.021	8.984	8.979	8.980	0.074	0.066	0.067	0.000	0.000	0.000
14	0.005	0.014	0.013	9.404	9.428	9.427	0.152	0.120	0.123	0.000	0.000	0.000
15	0.003	0.009	0.008	9.691	9.773	9.767	0.293	0.206	0.212	0.000	0.000	0.000
16	0.002	0.006	0.005	9.873	10.044	10.031	0.517	0.343	0.357	0.000	0.000	0.000
17	0.001	0.004	0.003	9.959	10.238	10.215	0.845	0.566	0.590	0.000	0.000	0.000
18	0.001	0.002	0.002	9.936	10.315	10.281	1.300	0.923	0.958	0.000	0.000	0.000
19	0.000	0.001	0.001	9.780	10.217	10.175	1.925	1.491	1.533	0.000	0.000	0.000
20	0.000	0.001	0.001	9.464	9.892	9.850	2.756	2.332	2.374	0.000	0.000	0.000
21	0.000	0.001	0.000	8.977	9.341	9.306	3.804	3.444	3.479	0.000	0.000	0.000
22	0.000	0.000	0.000	8.337	8.618	8.592	5.042	4.764	4.790	0.000	0.000	0.000
23	0.000	0.000	0.000	7.528	7.727	7.708	6.515	6.318	6.336	0.000	0.000	0.000
24	0.000	0.000	0.000	6.390	6.511	6.500	8.505	8.385	8.396	0.000	0.000	0.000
25	0.000	0.000	0.000	5.022	5.084	5.078	10.838	10.776	10.782	0.000	0.000	0.000
26	0.000	0.000	0.000	3.744	3.774	3.771	12.985	12.955	12.958	0.000	0.001	0.001
27	0.000	0.000	0.000	2.639	2.654	2.652	14.827	14.812	14.813	0.001	0.002	0.001
28	0.000	0.000	0.000	1.838	1.846	1.845	16.156	16.147	16.149	0.001	0.003	0.002
29	0.000	0.000	0.000	1.234	1.239	1.238	17.157	17.149	17.150	0.002	0.004	0.004
30	0.000	0.000	0.000	0.802	0.807	0.806	17.871	17.862	17.864	0.003	0.007	0.006

a) Concentrations in g/L. Data computed for the mixtures listed in Table 4-1.

Figure 4-2. Species concentrations as a function of pH_{act}. The color of the line designates the identity of the species (see legend). Concentrations calculated without ionic strength considerations ($f = 1$) are shown as solid lines and those calculated with the activity coefficients from the Davies equation with $b = 0.1$ are shown as dashed lines. The black curves show the ionic strength of the equilibrium solutions and are plotted with respect to the secondary axis.

Figure 4-2 shows the non- H^+ species concentrations as functions of pH_{act} . The H_nCit^{n-3} and $H_mPO_4^{m-3}$ species are plotted on top and bottom, respectively. The plots in Figure 4-2 show that the concentration maxima occur at significantly different pH values for the $f = 1$ (solid) and Davies, (dashed) data sets. Since the $b = 0.1$ and $b = 0.2$ data sets give exactly the same curves, only the $b = 0.1$ data set is shown in Figure 4-2.

The H_3Cit concentration starts at about 16 g/L for the most acidic solution studied and decreases as the fraction of HPO_4^{2-} increases. As the solution becomes more basic, one observes maxima for the concentrations of the conjugate bases: $[H_2Cit^-]$ at $pH \approx 4.0$ ($f = 1$) or 3.4 (Davies), $[HCit^{2-}]$ at $pH \approx 5.6$ ($f = 1$) or 4.8 (Davies), and $[Cit^{3-}]$ at $pH \approx 7.0$ ($f = 1$) or 6.2 (Davies).

High concentrations of HPO_4^{2-} occur at high pH. Even at the most basic pH values studied, only a small fraction of HPO_4^{2-} is deprotonated. Thus, the $[PO_4^{3-}]$ curve essentially lies on the pH_{act} axis and $[PO_4^{3-}]$ never reaches 0.01 g/L. As the fraction of citric acid increases, the pH decreases and HPO_4^{2-} is protonated. The concentration of $H_2PO_4^-$ is highest at $pH \approx 6.4$ ($f = 1$) or 5.6 (Davies). Further protonation of $H_2PO_4^-$ occurs only to a small extent and $H_2PO_4^-$ remains the dominant $H_mPO_4^{m-3}$ species in solution. The concentration of neutral H_3PO_4 only goes through a shallow maximum at $pH \approx 2.9$ ($f = 1$) or 2.7 (Davies).

Figure 4-2 demonstrates in a compelling fashion the importance of ionic strength on the distribution of species at equilibrium. The positions of the maxima of the solid ($f = 1$) and dashed (Davies) curves can be separated by almost an entire pH unit! Since the concentration of any species typically decreases rapidly as the pH shifts from the value its concentration is maximized, small differences in pH can have drastic effects on the equilibrium distribution of species.

Table 4-3. Concentration Differences (g/L) for $f = 1$ and Davies Data at Select pH Values

	Species, S	$[S, f = 1]$	$[S, b = 0.1]$	Δ (%)
pH = 4.7	H_2Cit^-	6.50	2.68	-83.3
	HCit^{2-}	4.37	6.46	+38.6
	Cit^{3-}	0.00	0.95	+200.0
	H_2PO_4^-	7.86	9.31	+16.9
pH = 6.3	HCit^{2-}	5.32	1.14	-129.4
	Cit^{3-}	2.65	5.29	+66.7
	H_2PO_4^-	10.18	8.83	-14.3
	HPO_4^-	1.06	4.32	+121.4

Numerical data for the specific cases at pH 4.7 and 6.3 are provided in Table 4-3. The last column in Table 4-3 shows the percentage change and the direction of the change of the concentration of species S associated with inclusion of the activity effects; $\Delta = 100 \cdot ([S, b = 0.1] - [S, f = 1]) / (0.5 \cdot ([S, b = 0.1] + [S, f = 1]))$. Wide discrepancies are apparent for the two models and the percent differences, Δ , range from 14.3 % to 200.0 %. Clearly, the inclusion of ionic strength effects is vital to the accurate determination of equilibrium species distribution at a given pH.

A second practical application of Figure 4-2 concerns the determination of the optimal pH to achieve a relative maximum of a desired ionic species. For example, the $f = 1$ curve in Figure 4-2 would suggest that the optimum pH to maximize $[\text{H}_2\text{PO}_4^-]$ would be 6.5. However, when ionic strength effects are included, one finds that at pH = 6.5 the concentration of the H_2PO_4^- ion would only be about 75% of the maximum value and the solution would have approximately a 1:3 ratio of $[\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$. The appropriate pH to maximize $[\text{H}_2\text{PO}_4^-]$ and diminish interference from its conjugate base is 5.4 as given by the Davies curve. Conversely, to directly compare the ability of a receptor to selectively bind $[\text{H}_2\text{PO}_4^-]$ over $[\text{HPO}_4^{2-}]$, one should select a pH where both of these species exist in similar quantities. An appropriate pH for such a

measurement would not be 7.5, as suggested by the $f = 1$ curve, but 6.8, as suggested by the Davies curve.

4.4.3. Ionic Strength Dependence of Concentration Quotients and Thermodynamic Equilibrium Constants

Generally, for the y -th dissociation of an m -protic acid H_mA , the concentration quotient Q_y is given by eq. 21. In more concentrated solutions, eq. 21 needs to be replaced by the corresponding expression for the thermodynamic equilibrium constants $K_{y,act}$ (eq. 22) in which all concentrations $[S]$ are replaced by activities $a(S)$.

$$Q_y = [H^+][H_{m-y}A^{-y}] / [H_{m-y+1}A^{1-y}] \quad (21)$$

$$K_{y,act} = f_1[H^+] a(H_{m-y}A^{-y}) / a(H_{m-y+1}A^{1-y}) \quad (22)$$

$$K_y = \lim_{I \rightarrow 0} Q_y \quad (23)$$

$$K_y = K_{y,act} \text{ for all } I \quad (24)$$

$$D = A \left(\frac{\sqrt{I}}{1+\sqrt{I}} - b I \right) \quad (25)$$

Insertion of eq. 2 into eq. 22 and using the abbreviation of eq. 25, one arrives at eq. 26 which relates the concentration quotient Q_y to the thermodynamic equilibrium constant $K_{y,act}$.

$$K_{y,act} = Q_y \cdot \{ 10^{(2y \cdot D)} \} \quad (26)$$

At infinite dilution, activities and concentrations become equal and the equilibrium coefficient K_y equals the concentration quotient Q_y (eq. 23). It is well established that the concentration quotients Q_y do not equal K_y even at low ionic strength.^{47,67} Yet, all the calculations employ the numerical value of K_y for all I . It is a direct consequence of this practice that eq. 24 must hold for all I , that is, that the equilibrium constants K_y equal the thermodynamic equilibrium constants $K_{y,act}$ not just in the limit of infinite dilution but in the entire range of ionic strength being modeled with Debye-Hückel theory.

$$Q_{1y} = [H^+][H_{3-y}A^{-y}] / [H_{4-y}A^{1-y}] \quad (27a)$$

$$Q_{2y} = [H^+][H_{3-y}B^{-y}] / [H_{4-y}B^{1-y}] \quad (27b)$$

$$K_{1y,act} = f_1[H^+] a(H_{3-y}A^{-y}) / a(H_{4-y}A^{1-y}) \quad (28a)$$

$$K_{2y,act} = f_1[H^+] a(H_{3-y}B^{-y}) / a(H_{4-y}B^{1-y}) \quad (28b)$$

Previously, we plotted the concentration quotients Q_{xy} for two systems (acetate-buffered acetic acid; titration of citric acid with sodium hydroxide) using several approximations of Debye-Hückel theory and showed that pQ_y is always less than pK_y and that the difference between them increases nonlinearly as ionic strength increases.⁷ Ganesh et al. recently reported a similar finding for a universal buffer system.⁶⁸ We show an example of this kind of plot in Figure 4-6 (Appendix) for the first dissociation of citric acid in the buffer system.

(a)

(b)

Figure 4-3. Comparison of the equilibrium coefficient expressions (eqs. 21 & 22) for the dissociations of (a) citric acid and (b) phosphoric acid in the mixtures. Line color distinguishes between $pK_{xy,conc}$ (green), $pK_{xy,act}$ (blue), and pK_{xy} (red). Solid: $b = 0.1$; dashed: $b = 0.2$. The $pK_{xy,act}$ lines are also marked with circles for improved visibility.

The concentration quotients Q_{xy} were computed for all of the equilibria in the buffer system using eqs. 27a and 27b and the concentrations in Tables 4.2a and 4.2b. Figure 4-3 shows the pQ_{xy} curves as functions of ionic strength for citric acid ($x = 1$, left) and phosphoric acid ($x = 2$, right). As before, red horizontal lines show the pK_{xy} values at infinite dilution. The pQ_{xy} curves for all data always are less than the pK_{xy} values at infinite dilution, the difference grows nonlinearly as I increases, as expected, and the deviation always is larger for the $b = 0.1$ data (solid curves) than for the $b = 0.2$ data (dashed curves) for these systems. Also, for any given ionic strength, the difference between the equilibrium constants and the concentration quotients $pK_{xy} - pQ_{xy}$ increases from the first dissociation ($y = 1$), to the second dissociation ($y = 2$), and again to the third dissociation ($y = 3$). This trend is also expected because the z^2 dependency of the f values is more pronounced in the curves of the higher order dissociations.

We also calculated the thermodynamic equilibrium constants $K_{xy,act}(I)$ using eqs. 28a and 28b with the concentrations from Tables 4.2a and 4.2b and the activity coefficients from the Davies equation for both $b = 0.1$ and $b = 0.2$ and the results are included in Figure 4-3 as blue marks. These $pK_{xy,act}(I)$ values all align with the pK_{xy} values at infinite dilution (red lines). This outcome of the numerical solution of the ODE systems is required by eq. 24 and Figure 4-3 thus validates the numerical accuracy of the dynamical approach to multi-equilibria system.

4.4.4. Attempted Speciation of Citric Acid via ^1H NMR Spectroscopy

The geminal hydrogens of the two equivalent CH_2 groups are diastereotopic and the AB spin system gives rise to two doublets with the same coupling constant $^2J_{AB}$.⁶⁹ We measured the ^1H NMR spectra of a dilute aqueous solution of potassium citrate (5.36 mg of K_3Cit in 100 mL H_2O) as a function of pH by adding small aliquots of 3M H_2SO_4 . Spectra were recorded on a

600 MHz Bruker Avance III spectrometer using water suppression techniques, and a typical spectrum is shown in the Appendix together with a table of the chemical shifts of the four peaks at each pH (Figure 4-7 and Table 4-8). The doublets show $^2J = 15.3 \pm 0.4$ Hz and the chemical shifts of the centers of the doublets are shown in Figure 4-4 as a function of pH.

Figure 4-4. ^1H NMR shifts relative to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid) for citric acid in 90% H_2O : 10% D_2O over the pH range 2 – 9.

Each apparent methylene proton signal δ_{H} corresponds to the average of the chemical shifts of all protonation states of the species in solution, and a first approximation of δ_{H} is given by the equation

$$\delta_{\text{H}} = \sum_{i=0}^3 c_i \times \delta_{\text{H}}(\text{H}_i\text{Cit}^{i-3}), \quad (29)$$

where c_i are the concentrations of the species i , and $\delta_{\text{H}}(\text{H}_i\text{Cit}^{i-3})$ are the chemical shifts of the respective methylene-H of the individual species. If this equation holds and if the $\delta_{\text{H}}(\text{H}_i\text{Cit}^{i-3})$ values are known, then one should be able to obtain speciation information from eq. 29 (i.e., the

c_i values). Values for the individual chemical shifts $\delta_{\text{H}}(\text{H}_3\text{Cit})$ and $\delta_{\text{H}}(\text{Cit}^{3-})$ can be determined experimentally by adding excess acid to an aqueous citrate solution. The $\delta_{\text{H}}(\text{H}_3\text{Cit})$ values for the two diastereotopic hydrogens are 2.84 (A) and 3.01 ppm (B) and the $\delta_{\text{H}}(\text{Cit}^{3-})$ values are 2.53 (A) and 2.63 ppm (B), respectively (Figure 4-4). However, the individual shifts $\delta(\text{H}_2\text{Cit}^-)$ and $\delta(\text{HCit}^{2-})$ cannot be determined in “pure” solutions of the respective anions. Instead of gaining reliable speciation information from the chemical shift measurements, the best one can hope for is an additional constraint in a simultaneous fitting process of $\text{pH} = f(c_i)$ and of $\delta_{\text{H}} = f(c_i)$ with a given theoretical model for the treatment of the electrolyte solution that includes the values $\delta(\text{H}_2\text{Cit}^-)$ and $\delta(\text{HCit}^{2-})$ as variables. In any case, such attempts cannot be expected to fully succeed because eq. 29 assumes that the chemical shift $\delta_{\text{H}}(\text{H}_i\text{Cit}^{i-3})$ of each species is independent of pH and the changing chemical environment. However, in related studies we and others found that pH effects on chemical shifts can be quite large (up to 0.1 ppm).⁷⁰

4.4.5. Further Applications and Desiderata

The simulations of the pH profiles (Figure 4-1) shows that the $b = 0.1$ data achieve the best match with experiment. It would be desirable to assess the quality of a specific Debye-Hückel approximation not just on the concentration of *one* species (pH) but on the concentration dependence of *several* species. This seems particularly well advised in cases where the only measured species is present in very low concentration. From our perspective, it would be highly desirable and instructive to simulate complex multi-equilibria systems for which the concentrations of *several* species were measured simultaneously and over a broad pH range. Ideally, the measured species should include systems containing multiply-charged ions in significant concentrations.

In the present study, we employed equilibrium constants at infinite dilution K_{xy} and the Davies equation with two discrete b values. Comparison of computed and measured pH values then suggested which b value resulted in better agreement. If one had experimental data for more species, i.e., some of the ions $H_{3-y}A^{-y}$ and $H_{3-y}B^{-y}$ in the present example, then one would have much tougher constraints on the precise formulation of the DH approximation. Moreover, instead of using $K_{xy,\infty} \neq f(I)$, one would also be in a position to explore effects of $K_{xy,act}$ *via* iterative setting of $K_{xy,act} = f(I)$ together with the determination of the activity coefficients (eq. 2) in the process of solving the ODEs. In the range $0 \leq I \leq 0.6$, changes of the pK_a values up to 0.29 and 0.25 units were reported for citric acid and phosphoric acid, respectively,⁵⁶ and these data inform about the shape of trial functions $K_{xy,act} = f(I)$. For the present case, Figure 4-2 (bottom) suggests that precise measurements of $[HCit^{2-}]$ and pH in the range $4 \leq pH \leq 6.5$ would allow one to test such approaches and their effects on the shape of the $[H_2PO_4^-] = f(pH)$ curves.

One further application of the dynamical approach is the indirect determination of accurate binding constants, K_b , for specific ion receptors in aqueous media.^{14,30} The dynamical method allows for the facile inclusion of receptor terms $R[t]$ and $RIA[t]$ to describe the concentrations of the receptor and the receptor-ion aggregate, respectively. With these additions, a simple comparison to the experimental pH profile would allow one to estimate the K_b for the receptor. Such simple determination of binding constants would be invaluable to studies where direct observation of the aggregating species concentrations is difficult or impossible. And even in cases where direct determination of the formation constant is possible, this approach may facilitate the study of the ionic strength dependence of K_b .

4.5. Conclusion

The dynamical approach was employed to describe the complex multi-equilibria buffer system of citric acid and disodium hydrogen phosphate and the experimental pH profile was modeled with astounding accuracy. The effects of ionic strength were shown to be highly important for the calculation of the pH and the model suggests that the non- H^+ species concentrations are affected by ionic strength effects to an even greater extent. We presented a few examples of common scenarios where neglecting the ionic strength effects would drastically effect the equilibrium species distribution and, therefore, knowledge of the extent of ionic strength effects is essential. We also presented an application for the dynamical approach in the indirect determination of binding constants as functions of ionic strength, which has an immediate and practical use for researchers developing new chemical sensors.

Improvement to the dynamical approach could involve concomitant improvements to approximations of Debye-Hückel theory. The Davies approximation was tested here with the empirical parameters $b = 0.1$ and $b = 0.2$ and we have shown that the $b = 0.1$ data matches more closely with experiment. This can be extended to other approximations, such as the Pitzer equation,^{46,71} to see if increased accuracy is attained in the calculation of $[\text{H}^+]$. We note that experimental data sets in which concentration profiles for two or more species are monitored would greatly enhance the confidence in the results obtained with the dynamical approach and thereby provide an excellent system to systematically test the extensions to Debye-Hückel theory.

4.6. References

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4.7. Appendix

Figure 4-5. Examples of selective optical sensors for detection H_2PO_4^- . Red circles indicate the binding site of H_2PO_4^- .

Comparison to Equilibrium Method

We compared the results obtained with the dynamical approach to the result computed with the equilibrium approach via the iterative solution of the equilibrium equations with the add-in *Solver* tool in Microsoft Excel.^{4,5} To fully describe the equilibria one needs at least as many equations as there are *species* in the solution. The number of species exceeds the number of equilibrium equations and balance equations are needed to make up for the difference. There is one mass balance equation for acid H₃A and its conjugate bases and a second mass balance equation for acid H₃B and its conjugate bases. Also, there is one charge balance equation.

Four convenient “variables” were chosen and they are: IS, [H⁺], [H₃A], and [HB²⁻]. The initial conditions, pK_a values, and the Davies equations (with $b = 0.1$) for the activity coefficients were all specified and all other species concentrations were thus defined algebraically in terms of the four variables. An error function is expressed as the difference between the mathematical definition of the parameter and the current value that parameter. The magnitude of the value in the “balance equation cell” is a measure of how far the system is from equilibrium. The composite error function employed here is defined as the sum of the errors of the balance equations and of the ionic strength error function. Each individual error function is squared to maintain a positive value. The composite error function is advantageous because it includes many of the ionic species and this sensitivity allows for faster and smoother convergence to the equilibrium. The composite error cell is used as the objective cell in the *Solver* tool and is minimized via manipulation of the variable cells.

After running the *Solver* tool, some of the data generated were not physically realistic (e.g., the sum of output concentrations of all A-containing species exceeded [H₃A]₀). Therefore, the following constraints were added to the *Solver* tool: (1) H_{inp} = H_{out}, (2) A_{inp} = A_{out}, (3) B_{inp} = B_{out}, (4) IS > 0, where A_{inp} is equal to [H₃A]₀, B_{inp} is [HB²⁻]₀, and H_{inp} is $3 \times [\text{H}_3\text{A}]_0 + [\text{HB}^{2-}]_0 + [\text{H}^+]_0$ and A_{out} is [H₃A] + [H₂A⁻] + [HA²⁻] + [A³⁻] and similarly for B_{out} and H_{out}. With these additional inputs, the calculated pH_{act} is in good agreement with the results of the dynamical

approach and with experiment. Tables 4-1 and 4-4 and 4-6 include pH values obtained with this method.

The method is helpful because it numerically approximates the pH, but it is pragmatically unsophisticated; non-variable species concentrations and balance equations are defined and computed algebraically, and the user must perform all of the algebra and cell-selecting. This is not trivial because it means that expanding the method or describing a new system/adding a new species involves reconstruction of a major portion of the spreadsheet. Also, results are obtained one at a time with no scalability for large data sets, making recalculation for new or adjusted systems rather tedious.

Figure 4-6. Negative logarithm of the concentration quotient, pQ_1 (green) for the first dissociation of citric acid shown as a function of ionic strength and compared to the pK_a at infinite dilution, pK_1 (red), using the data for the citric acid/hydrogenphosphate mixtures. The pQ_1 curve begins at $IS = 0.05$ M which corresponds to the most acidic mixture studied.

Table 4-4. Reported and Calculated pH values and Ionic Strength for a Series of Mixtures^a of the Buffer Solution

Mix.	[H ₃ Cit] ₀	[HPO ₄ ²⁻] ₀	Expt. ⁸	$f = 1$		$b = 0.1$		$b = 0.2$		Lit. ^b	Ionic Strength		
	[mol/L]	[mol/L]	pH	pH _{conc}	pH _{act}	pH _{conc}	pH _{act}	pH _{conc}	pH _{act}	pH _{act}	$f = 1$	$b = 0.1$	$b = 0.2$
1	0.098	0.004	2.2	2.25	2.30	2.18	2.23	2.18	2.23	2.23	0.01	0.01	0.01
2	0.094	0.012	2.4	2.53	2.60	2.41	2.48	2.41	2.48	2.48	0.03	0.03	0.03
3	0.089	0.022	2.6	2.77	2.86	2.61	2.70	2.61	2.70	2.70	0.05	0.05	0.05
4	0.084	0.032	2.8	3.00	3.10	2.80	2.90	2.80	2.90	2.90	0.07	0.07	0.07
5	0.079	0.041	3.0	3.21	3.32	2.98	3.09	2.99	3.09	3.09	0.08	0.09	0.09
6	0.075	0.049	3.2	3.41	3.53	3.15	3.26	3.16	3.27	3.26	0.10	0.10	0.10
7	0.072	0.057	3.4	3.63	3.75	3.32	3.45	3.34	3.45	3.45	0.12	0.12	0.12
8	0.068	0.064	3.6	3.89	4.01	3.51	3.64	3.53	3.66	3.64	0.14	0.14	0.14
9	0.065	0.071	3.8	4.15	4.28	3.70	3.84	3.73	3.86	3.84	0.15	0.16	0.16
10	0.061	0.077	4.0	4.40	4.53	3.89	4.03	3.92	4.05	4.03	0.17	0.17	0.17
11	0.059	0.083	4.2	4.63	4.77	4.07	4.22	4.11	4.25	4.22	0.19	0.19	0.19
12	0.056	0.088	4.4	4.87	5.01	4.26	4.41	4.31	4.44	4.41	0.21	0.21	0.21
13	0.053	0.094	4.6	5.13	5.27	4.47	4.62	4.52	4.66	4.62	0.23	0.23	0.23
14	0.051	0.099	4.8	5.42	5.57	4.69	4.85	4.75	4.89	4.85	0.25	0.25	0.25
15	0.049	0.103	5.0	5.70	5.84	4.90	5.06	4.96	5.11	5.06	0.27	0.27	0.27
16	0.046	0.107	5.2	5.93	6.08	5.09	5.26	5.17	5.32	5.26	0.29	0.29	0.29
17	0.044	0.112	5.4	6.14	6.29	5.29	5.46	5.37	5.52	5.46	0.31	0.31	0.31
18	0.042	0.116	5.6	6.33	6.48	5.49	5.66	5.57	5.73	5.66	0.33	0.33	0.33
19	0.040	0.121	5.8	6.51	6.66	5.69	5.86	5.78	5.93	5.86	0.35	0.35	0.35
20	0.037	0.126	6.0	6.68	6.83	5.89	6.06	5.98	6.13	6.06	0.37	0.37	0.37
21	0.034	0.132	6.2	6.84	7.00	6.08	6.25	6.16	6.32	6.25	0.39	0.39	0.39
22	0.031	0.139	6.4	7.00	7.15	6.24	6.42	6.33	6.49	6.42	0.41	0.41	0.41
23	0.027	0.146	6.6	7.15	7.31	6.41	6.59	6.50	6.65	6.59	0.43	0.43	0.43
24	0.023	0.155	6.8	7.34	7.50	6.59	6.78	6.69	6.85	6.78	0.46	0.46	0.46
25	0.018	0.165	7.0	7.55	7.71	6.80	6.98	6.90	7.06	6.98	0.49	0.49	0.49
26	0.013	0.174	7.2	7.75	7.92	7.00	7.19	7.11	7.27	7.19	0.52	0.52	0.52
27	0.009	0.182	7.4	7.96	8.13	7.21	7.39	7.32	7.48	7.39	0.54	0.55	0.54
28	0.006	0.187	7.6	8.16	8.32	7.40	7.59	7.51	7.67	7.59	0.56	0.56	0.56
29	0.004	0.192	7.8	8.36	8.52	7.59	7.78	7.71	7.87	7.78	0.57	0.57	0.57
30	0.003	0.195	8.0	8.56	8.72	7.80	7.99	7.91	8.08	7.99	0.58	0.58	0.58

a) Volumes of buffer solutions given in ref. 8 were converted to concentrations and used as initial values in the various approaches.

b) Calculated using the method described in ref. 5 with modifications.

Table 4-5a. Calculated Citrate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ Cit]			[H ₂ Cit ⁻]			[HCit ²⁻]			[Cit ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	86.6	85.7	85.7	11.4	12.3	12.2	0.0	0.1	0.1	0.0	0.0	0.0
2	74.9	74.1	74.1	18.8	19.6	19.5	0.1	0.2	0.2	0.0	0.0	0.0
3	61.6	61.1	61.1	27.2	27.6	27.6	0.3	0.4	0.4	0.0	0.0	0.0
4	48.0	47.8	47.8	35.5	35.4	35.4	0.6	1.0	1.0	0.0	0.0	0.0
5	35.6	35.8	35.8	42.7	41.8	41.8	1.2	1.9	1.9	0.0	0.0	0.0
6	25.1	25.8	25.7	48.1	46.2	46.3	2.2	3.3	3.3	0.0	0.0	0.0
7	16.2	17.5	17.5	51.4	48.4	48.5	3.8	5.6	5.5	0.0	0.0	0.0
8	9.1	10.8	10.7	51.8	47.8	48.1	6.9	9.1	8.9	0.0	0.1	0.1
9	4.6	6.3	6.2	48.1	44.3	44.6	11.7	13.7	13.5	0.1	0.2	0.2
10	2.2	3.5	3.4	41.2	38.5	38.7	17.9	19.1	19.0	0.2	0.4	0.4
11	1.0	1.8	1.8	32.7	31.3	31.4	24.5	24.6	24.6	0.4	0.9	0.8
12	0.4	0.9	0.8	23.9	23.6	23.6	30.7	29.7	29.8	0.9	1.7	1.6
13	0.2	0.4	0.3	15.3	16.0	15.9	35.9	33.6	33.8	1.9	3.3	3.2
14	0.0	0.1	0.1	8.3	9.6	9.5	38.3	34.9	35.2	4.1	6.0	5.8
15	0.0	0.0	0.0	4.3	5.6	5.4	36.9	33.3	33.6	7.3	9.6	9.4
16	0.0	0.0	0.0	2.2	3.0	2.9	32.9	29.4	29.7	11.2	13.9	13.7
17	0.0	0.0	0.0	1.1	1.5	1.5	27.7	24.0	24.4	15.4	18.7	18.4
18	0.0	0.0	0.0	0.6	0.7	0.7	22.3	18.2	18.6	19.1	23.1	22.7
19	0.0	0.0	0.0	0.3	0.3	0.3	17.2	12.7	13.1	22.1	26.6	26.1
20	0.0	0.0	0.0	0.2	0.1	0.1	12.7	8.3	8.7	24.0	28.4	28.0
21	0.0	0.0	0.0	0.1	0.1	0.1	9.0	5.3	5.6	24.8	28.6	28.2
22	0.0	0.0	0.0	0.0	0.0	0.0	6.2	3.3	3.6	24.5	27.4	27.1
23	0.0	0.0	0.0	0.0	0.0	0.0	4.1	2.1	2.2	23.1	25.2	25.0
24	0.0	0.0	0.0	0.0	0.0	0.0	2.3	1.1	1.2	20.4	21.6	21.5
25	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.5	0.6	16.5	17.1	17.1
26	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.2	0.3	12.5	12.8	12.8
27	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	8.9	9.0	9.0
28	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	6.2	6.3	6.3
29	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2	4.2	4.2
30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.7	2.7	2.7

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table 4-4.

Table 4-5b. Calculated Phosphate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ PO ₄]			[H ₂ PO ₄ ⁻]			[HPO ₄ ²⁻]			[PO ₄ ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	1.8	1.7	1.7	2.2	2.3	2.3	0.0	0.0	0.0	0.0	0.0	0.0
2	3.7	3.6	3.6	8.7	8.8	8.8	0.0	0.0	0.0	0.0	0.0	0.0
3	4.3	4.2	4.2	17.5	17.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0
4	4.0	4.0	4.0	27.7	27.7	27.7	0.0	0.0	0.0	0.0	0.0	0.0
5	3.4	3.5	3.4	37.7	37.6	37.6	0.0	0.0	0.0	0.0	0.0	0.0
6	2.6	2.8	2.8	46.8	46.6	46.6	0.0	0.0	0.0	0.0	0.0	0.0
7	1.9	2.1	2.1	55.1	54.8	54.9	0.0	0.0	0.0	0.0	0.0	0.0
8	1.2	1.5	1.5	63.2	62.8	62.9	0.0	0.0	0.0	0.0	0.0	0.0
9	0.7	1.1	1.0	70.2	69.9	69.9	0.1	0.1	0.1	0.0	0.0	0.0
10	0.4	0.7	0.7	76.5	76.2	76.2	0.1	0.1	0.1	0.0	0.0	0.0
11	0.3	0.5	0.5	82.3	82.1	82.1	0.2	0.2	0.2	0.0	0.0	0.0
12	0.2	0.3	0.3	87.6	87.5	87.5	0.4	0.4	0.4	0.0	0.0	0.0
13	0.1	0.2	0.2	92.6	92.6	92.6	0.8	0.7	0.7	0.0	0.0	0.0
14	0.1	0.1	0.1	97.0	97.2	97.2	1.6	1.3	1.3	0.0	0.0	0.0
15	0.0	0.1	0.1	99.9	100.8	100.7	3.1	2.1	2.2	0.0	0.0	0.0
16	0.0	0.1	0.1	101.8	103.6	103.4	5.4	3.6	3.7	0.0	0.0	0.0
17	0.0	0.0	0.0	102.7	105.6	105.3	8.8	5.9	6.1	0.0	0.0	0.0
18	0.0	0.0	0.0	102.4	106.4	106.0	13.5	9.6	10.0	0.0	0.0	0.0
19	0.0	0.0	0.0	100.8	105.3	104.9	20.1	15.5	16.0	0.0	0.0	0.0
20	0.0	0.0	0.0	97.6	102.0	101.6	28.7	24.3	24.7	0.0	0.0	0.0
21	0.0	0.0	0.0	92.6	96.3	96.0	39.6	35.9	36.2	0.0	0.0	0.0
22	0.0	0.0	0.0	86.0	88.9	88.6	52.5	49.6	49.9	0.0	0.0	0.0
23	0.0	0.0	0.0	77.6	79.7	79.5	67.9	65.8	66.0	0.0	0.0	0.0
24	0.0	0.0	0.0	65.9	67.1	67.0	88.6	87.4	87.5	0.0	0.0	0.0
25	0.0	0.0	0.0	51.8	52.4	52.4	112.9	112.3	112.3	0.0	0.0	0.0
26	0.0	0.0	0.0	38.6	38.9	38.9	135.3	135.0	135.0	0.0	0.0	0.0
27	0.0	0.0	0.0	27.2	27.4	27.3	154.5	154.3	154.3	0.0	0.0	0.0
28	0.0	0.0	0.0	19.0	19.0	19.0	168.3	168.2	168.3	0.0	0.0	0.0
29	0.0	0.0	0.0	12.7	12.8	12.8	178.8	178.7	178.7	0.0	0.0	0.0
30	0.0	0.0	0.0	8.3	8.3	8.3	186.2	186.1	186.1	0.0	0.1	0.1

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table 4-4.

Table 4-6. Reported and Calculated pH values and Ionic Strength for a Series of Mixtures^a of the Buffer Solution

Mix.	[H ₃ Cit] ₀	[HPO ₄ ²⁻] ₀	Expt. ⁹	$f = 1$		Davies		Lit. ^b	Ionic Strength	
	[mol/L]	[mol/L]	pH	pH _{conc}	pH _{act}	pH _{conc}	pH _{act}	pH _{act}	$f = 1$	Davies
1	0.089	0.022	2.6	2.77	2.86	2.61	2.70	2.70	0.05	0.05
2	0.084	0.032	2.8	3.00	3.10	2.80	2.90	2.90	0.07	0.07
3	0.079	0.041	3.0	3.21	3.32	2.98	3.09	3.09	0.08	0.09
4	0.075	0.049	3.2	3.41	3.53	3.15	3.26	3.26	0.10	0.10
5	0.072	0.057	3.4	3.63	3.75	3.32	3.45	3.45	0.12	0.12
6	0.068	0.064	3.6	3.89	4.01	3.51	3.64	3.64	0.14	0.14
7	0.065	0.071	3.8	4.15	4.28	3.70	3.84	3.84	0.15	0.16
8	0.061	0.077	4.0	4.40	4.53	3.89	4.03	4.03	0.17	0.17
9	0.059	0.083	4.2	4.63	4.77	4.07	4.22	4.22	0.19	0.19
10	0.056	0.088	4.4	4.87	5.01	4.26	4.41	4.41	0.21	0.21
11	0.053	0.094	4.6	5.13	5.27	4.47	4.62	4.62	0.23	0.23
12	0.051	0.099	4.8	5.42	5.57	4.69	4.85	4.85	0.25	0.25
13	0.049	0.103	5.0	5.70	5.84	4.90	5.06	5.06	0.27	0.27
14	0.046	0.107	5.2	5.93	6.08	5.09	5.26	5.26	0.29	0.29
15	0.044	0.112	5.4	6.14	6.29	5.29	5.46	5.46	0.31	0.31
16	0.042	0.116	5.6	6.33	6.48	5.49	5.66	5.66	0.33	0.33
17	0.040	0.121	5.8	6.51	6.66	5.69	5.86	5.86	0.35	0.35
18	0.037	0.126	6.0	6.68	6.83	5.89	6.06	6.06	0.37	0.37
19	0.034	0.132	6.2	6.84	7.00	6.08	6.25	6.25	0.39	0.39
20	0.031	0.139	6.4	7.00	7.15	6.24	6.42	6.42	0.41	0.41
21	0.027	0.146	6.6	7.15	7.31	6.41	6.59	6.59	0.43	0.43
22	0.023	0.155	6.8	7.34	7.50	6.59	6.78	6.78	0.46	0.46
23	0.018	0.165	7.0	7.55	7.71	6.80	6.98	6.98	0.49	0.49
24	0.013	0.174	7.2	7.75	7.92	7.00	7.19	7.19	0.52	0.52
25	0.009	0.182	7.4	7.96	8.13	7.21	7.39	7.39	0.54	0.55

a) Volumes of buffer solutions given in ref. 9 were converted to concentrations and used as initial values in the various approaches.

b) Calculated using the method described in ref. 5 with modifications.

Table 4-7a. Calculated Citrate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ Cit]			[H ₂ Cit ⁻]			[HCit ²⁻]			[Cit ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	61.6	61.1	61.1	27.2	27.6	27.6	0.3	0.4	0.4	0.0	0.0	0.0
2	48.0	47.8	47.8	35.5	35.4	35.4	0.6	1.0	1.0	0.0	0.0	0.0
3	35.6	35.8	35.8	42.7	41.8	41.8	1.2	1.9	1.9	0.0	0.0	0.0
4	25.1	25.8	25.7	48.1	46.2	46.3	2.2	3.3	3.3	0.0	0.0	0.0
5	16.2	17.5	17.5	51.4	48.4	48.5	3.8	5.6	5.5	0.0	0.0	0.0
6	9.1	10.8	10.7	51.8	47.8	48.1	6.9	9.1	8.9	0.0	0.1	0.1
7	4.6	6.3	6.2	48.1	44.3	44.6	11.7	13.7	13.5	0.1	0.2	0.2
8	2.2	3.5	3.4	41.2	38.5	38.7	17.9	19.1	19.0	0.2	0.4	0.4
9	1.0	1.8	1.8	32.7	31.3	31.4	24.5	24.6	24.6	0.4	0.9	0.8
10	0.4	0.9	0.8	23.9	23.6	23.6	30.7	29.7	29.8	0.9	1.7	1.6
11	0.2	0.4	0.3	15.3	16.0	15.9	35.9	33.6	33.8	1.9	3.3	3.2
12	0.0	0.1	0.1	8.3	9.6	9.5	38.3	34.9	35.2	4.1	6.0	5.8
13	0.0	0.0	0.0	4.3	5.6	5.4	36.9	33.3	33.6	7.3	9.6	9.4
14	0.0	0.0	0.0	2.2	3.0	2.9	32.9	29.4	29.7	11.2	13.9	13.7
15	0.0	0.0	0.0	1.1	1.5	1.5	27.7	24.0	24.4	15.4	18.7	18.4
16	0.0	0.0	0.0	0.6	0.7	0.7	22.3	18.2	18.6	19.1	23.1	22.7
17	0.0	0.0	0.0	0.3	0.3	0.3	17.2	12.7	13.1	22.1	26.6	26.1
18	0.0	0.0	0.0	0.2	0.1	0.1	12.7	8.3	8.7	24.0	28.4	28.0
19	0.0	0.0	0.0	0.1	0.1	0.1	9.0	5.3	5.6	24.8	28.6	28.2
20	0.0	0.0	0.0	0.0	0.0	0.0	6.2	3.3	3.6	24.5	27.4	27.1
21	0.0	0.0	0.0	0.0	0.0	0.0	4.1	2.1	2.2	23.1	25.2	25.0
22	0.0	0.0	0.0	0.0	0.0	0.0	2.3	1.1	1.2	20.4	21.6	21.5
23	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.5	0.6	16.5	17.1	17.1
24	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.2	0.3	12.5	12.8	12.8
25	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	8.9	9.0	9.0

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table 4-6.

Table 4-7b. Calculated Phosphate Species Concentrations^a at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H ₃ PO ₄]			[H ₂ PO ₄ ⁻]			[HPO ₄ ²⁻]			[PO ₄ ³⁻]		
	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2	<i>f</i> = 1	<i>b</i> = 0.1	<i>b</i> = 0.2
1	4.3	4.2	4.2	17.5	17.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0
2	4.0	4.0	4.0	27.7	27.7	27.7	0.0	0.0	0.0	0.0	0.0	0.0
3	3.4	3.5	3.4	37.7	37.6	37.6	0.0	0.0	0.0	0.0	0.0	0.0
4	2.6	2.8	2.8	46.8	46.6	46.6	0.0	0.0	0.0	0.0	0.0	0.0
5	1.9	2.1	2.1	55.1	54.8	54.9	0.0	0.0	0.0	0.0	0.0	0.0
6	1.2	1.5	1.5	63.2	62.8	62.9	0.0	0.0	0.0	0.0	0.0	0.0
7	0.7	1.1	1.0	70.2	69.9	69.9	0.1	0.1	0.1	0.0	0.0	0.0
8	0.4	0.7	0.7	76.5	76.2	76.2	0.1	0.1	0.1	0.0	0.0	0.0
9	0.3	0.5	0.5	82.3	82.1	82.1	0.2	0.2	0.2	0.0	0.0	0.0
10	0.2	0.3	0.3	87.6	87.5	87.5	0.4	0.4	0.4	0.0	0.0	0.0
11	0.1	0.2	0.2	92.6	92.6	92.6	0.8	0.7	0.7	0.0	0.0	0.0
12	0.1	0.1	0.1	97.0	97.2	97.2	1.6	1.3	1.3	0.0	0.0	0.0
13	0.0	0.1	0.1	99.9	100.8	100.7	3.1	2.1	2.2	0.0	0.0	0.0
14	0.0	0.1	0.1	101.8	103.6	103.4	5.4	3.6	3.7	0.0	0.0	0.0
15	0.0	0.0	0.0	102.7	105.6	105.3	8.8	5.9	6.1	0.0	0.0	0.0
16	0.0	0.0	0.0	102.4	106.4	106.0	13.5	9.6	10.0	0.0	0.0	0.0
17	0.0	0.0	0.0	100.8	105.3	104.9	20.1	15.5	16.0	0.0	0.0	0.0
18	0.0	0.0	0.0	97.6	102.0	101.6	28.7	24.3	24.7	0.0	0.0	0.0
19	0.0	0.0	0.0	92.6	96.3	96.0	39.6	35.9	36.2	0.0	0.0	0.0
20	0.0	0.0	0.0	86.0	88.9	88.6	52.5	49.6	49.9	0.0	0.0	0.0
21	0.0	0.0	0.0	77.6	79.7	79.5	67.9	65.8	66.0	0.0	0.0	0.0
22	0.0	0.0	0.0	65.9	67.1	67.0	88.6	87.4	87.5	0.0	0.0	0.0
23	0.0	0.0	0.0	51.8	52.4	52.4	112.9	112.3	112.3	0.0	0.0	0.0
24	0.0	0.0	0.0	38.6	38.9	38.9	135.3	135.0	135.0	0.0	0.0	0.0
25	0.0	0.0	0.0	27.2	27.4	27.3	154.5	154.3	154.3	0.0	0.0	0.0

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table 4-6.

Figure 4-7. ^1H NMR spectrum of citric acid in 90% H_2O : 10% D_2O using a water suppression technique. The shifts for the citrate peak are given in Table 4-8 and the chemical shift of the water peak is 4.78 ppm.

Table 4-8. ^1H Chemical Shifts for Citric Acid in 90% H_2O : 10% D_2O (ppm relative to DSS)

pH	$\delta_{\text{H}}(\text{A}_1)$	$\delta_{\text{H}}(\text{A}_2)$	$\delta_{\text{H}}(\text{B}_1)$	$\delta_{\text{H}}(\text{B}_2)$
2.12	2.83	2.85	3.00	3.03
2.32	2.83	2.85	3.00	3.02
2.57	2.82	2.84	2.98	3.00
2.86	2.80	2.83	2.95	2.98
3.18	2.78	2.81	2.92	2.95
3.54	2.76	2.79	2.89	2.91
3.92	2.74	2.77	2.85	2.88
4.28	2.72	2.74	2.82	2.84
4.61	2.69	2.72	2.78	2.81
4.96	2.67	2.69	2.75	2.78
5.31	2.64	2.66	2.72	2.75
5.66	2.61	2.64	2.70	2.72
6.01	2.58	2.60	2.67	2.70
6.48	2.55	2.57	2.65	2.67
8.95	2.52	2.55	2.62	2.65

Chapter 5 The Dative Bonding Complex $\text{F}_3\text{B}\cdot\text{PH}_3$ Does Not Exist. The Microwave Spectrum Measured for the “ $\text{F}_3\text{B}\cdot\text{PH}_3$ Complex” Actually Shows $\text{F}_2\text{B}\cdot\text{PH}_2$

5.1. Introduction

Putative complexation between PH_3 and BF_3 has been debated for over a century. In 1890, Besson¹ wrote that mixing of gaseous PH_3 with BF_3 at -50°C (in the original “ $2\text{BoF}^3 + \text{PhH}^3$ ”) forms a white solid. Upon warming the solid becomes yellow and decomposes into PH_3 and 2 BF_3 and concomitant formation of higher phosphanes (P_nH_{n+2}) and H_2 gas. The reaction of the white solid with water liberated gaseous PH_3 .

In 1935, Egon Wiberg² reconsidered the aggregation between PH_3 and BF_3 at much lower temperatures (-130°C) to avoid decomposition and concluded that the low-temperature aggregate has the composition $\text{PH}_3\cdot\text{BF}_3$. Wiberg suggested that Besson’s “ $\text{PH}_3\cdot 2\text{BF}_3$ ” aggregate actually consisted of the “phosphonium borofluoride” $[\text{H}_3\text{P}(\text{BF}_2)][\text{BF}_4]$. Wiberg proposed that $\text{PH}_3\cdot\text{BF}_3$ condenses to difluoroborylphosphane $\text{H}_2\text{P}-\text{BF}_2$ and leads to difluoroborylphosphonium fluoride $[\text{H}_3\text{P}-\text{BF}_2]^+\text{F}^-$, the primary HF adduct of $\text{H}_2\text{P}-\text{BF}_2$. Further aggregation with BF_3 affords the difluoroborylphosphonium boron tetrafluoride $[\text{H}_3\text{P}-\text{BF}_2]^+[\text{BF}_4]^-$.

In 1950, Martin and Dial performed melting point analyses of frozen mixtures of BF_3 (m.p. $-127.0\pm 0.3^\circ\text{C}$) and PH_3 (m.p. $-133.0\pm 0.3^\circ\text{C}$) and molecular weight determinations of the gases in the head space.^{3,4} Freezing points of mixtures of BF_3 and PH_3 as a function of the BF_3 mole fraction were determined for mole fractions below 17.3% and above 84.1% BF_3 at pressures of about 8 atm. (In the range 17.3% - 84.1% BF_3 the solid mixture sublimed.) The data indicates the existence of two compounds with melting points of about -48°C (17.3% BF_3) and -83°C (84.1% BF_3). The molecular weight determinations are made at 0°C . Based on the measured mean molecular weights of these gases and the assumption that the gases contain only PH_3 , BF_3 ,

and $\text{H}_3\text{P}(\text{BF}_3)_n$ complexes, the authors concluded that the aggregates $\text{H}_3\text{P}\cdot\text{BF}_3$ and $\text{H}_3\text{P}(\cdot\text{BF}_3)_2$ can exist in the gas phase.

Durig attempted to measure ^1H and ^{11}B NMR spectra⁵ of the $\text{H}_3\text{P}\cdot\text{BF}_3$ system. Equimolar amounts of BF_3 and PH_3 were condensed into a 5 mm NMR tube, C_6D_6 was distilled onto the product at -196°C , and the NMR tube was flame sealed. NMR spectra taken at room temperature did not show any signals for the presumed adduct in solution. Durig noted that $\text{H}_3\text{P}\cdot\text{BCl}_3$ is known to interchange rapidly and this might also be true for $\text{H}_3\text{P}\cdot\text{BF}_3$. Durig was able to measure the vibrational spectrum for $\text{H}_3\text{P}\cdot\text{BF}_3$ in the solid state at -196°C . The IR and Raman spectra were rationalized with the assumption of C_{3v} symmetry and a generic set of structural parameters, and 11 of the 12 fundamental vibrations were assigned. Durig also noted that the vibrational spectra do not show any evidence for “ $\text{PH}_3\cdot 2\text{BF}_3$ ”.

In 1975, Odom measured microwave spectra of $\text{H}_3\text{P}\cdot\text{BF}_3$ and several of its isotopomers.⁶ Based on the measured rotational constants, with the assumption of C_{3v} symmetry, and with the geometry of the PH_3 moiety constrained, Odom was able to discern the other structural parameters (Table 5-1) and the dipole moment, 3.73 ± 0.30 D. In light of the dipole moment of $\text{H}_3\text{P}\cdot\text{BCl}_3$ (5.2 ± 0.1 D), the relatively low dipole moment was unexpected. The internal barrier to rotation was calculated via analysis of the torsional mode ($190 \pm 20 \text{ cm}^{-1}$) of the molecule and reported to be 3.34 ± 0.35 kcal/mol.

Several groups studied $\text{H}_3\text{P}\cdot\text{BF}_3$ with theoretical methods. Hirota⁷ studied the structure using restricted Hartree-Fock (RHF) theory and with the small 3-21G basis set. At the RHF/3-21G level the C_{3v} staggered structure is a minimum and its bond lengths and angles are very similar to the experimental results (Table 5-1). Alrichs⁸ used second-order Møller-Plesset perturbation theory (MP2) and the triple-zeta basis set with one set of polarization functions. Again, the C_{3v}

structure was identified as the minimum, but the geometry differed greatly from the structures by Hirota and Odom; in light of the computed B–P bond distance of 3.220 Å, Alrichs concluded that BF₃ and PH₃ were held together merely by “a weak van der Waals” interaction. Alrichs did observe a stationary structure with a shorter B–P bond in computations with the double-zeta basis set and considered this compact structure an artefact caused by basis set superposition errors⁹ (BSSE) in the small basis set computations. Subsequent computational work by Anane¹⁰ using the G2(MP2) procedure further corroborates the data from Alrichs. A binding energy of -2.96 kcal/mol was computed at the level QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d). From geometry considerations, Anane asserts that “there is probably no complex formation upon coordination between PH₃ and BF₃ moieties in the gas phase.”

Ford¹¹ studied the structure and the vibrational spectrum of the C_{3v}-symmetric F₃B·PH₃ complex at the MP2(full)/6-311++G(d,p) level. The computed vibrational data compared fairly well to the measurements by Durig⁵ (Table 5-5) with errors in the range of 3-10%. However, some outliers were observed. The calculated frequencies for both the symmetric and antisymmetric stretching modes of the B–F bonds were much greater than those reported by Durig while the frequency of the B–P stretching mode was much less than that of Durig. Ford suggested that these frequencies were merely incorrectly assigned. Ford also noted that the computed frequencies of the rocking modes (72, 190 cm⁻¹) are much lower than the measured fundamentals and basis set deficiencies were considered to be responsible for this discrepancy.

Very recently, Almas et al.¹² noticed that the potential energy surface (PES) of the dative bonded F₃B·PH₃ complex has a unique “shoulder” feature that is not present in similar, non-fluorinated structures. They explored the PES using several different method/basis set combinations, and

found that the shoulder persisted in each case. This suggests that two distinct dative-bonded minima may be possible in the case of the $\text{F}_3\text{B}\cdot\text{PH}_3$.

A summary of the geometrical parameters found in the literature is given in Table 5-1.

Table 5-1. The structure of F₃B·PH₃ at various levels.

Source	Bond Length (Å)			Bond Angle (°)				Dihed. (°)
	B–P	B–F	P–H	F–B–P	B–P–H	H–P–H	F–B–F	H–P–B–F
IR Spectrum (ref. 5)	1.960 ^a	1.380 ^a	1.400 ^a			101.0 ^a	114.0a	180.0 ^a
Microwave, (ref. 6)	1.921	1.372	1.400 ^a	106.7	117.0 ^a	101.1 ^a	112.1	180.0 ^a
SCF/3-21G, (ref. 7)	2.185	1.367	1.414	103.3	117.0	101.0	115.2	180.0
MP2/TZP, (ref. 8)	3.220	1.317	1.415	91.5	121.9	94.7	119.9	180.0
MP2(fu)/6-31G*, (ref. 9)	3.089	1.325	1.412	91.9	121.0	95.5	119.8	180.0
MP2(fu)/6-311++G**, (ref. 10)	3.075	1.322	1.407	92.4	121.3	95.6	119.8	180.0

^aConstrained by symmetry or assumed.

In this work, we suggest the difluoroborylphosphane complex, H_2PBF_2 , serves to reconcile the experimental work, especially the measured microwave spectrum with computational data. We will show that the primary data of the microwave study, the rotational constants, are in excellent agreement with the computed rotational constants of $\text{F}_2\text{B}-\text{PH}_2$, especially when compared to the dative bonded complex $\text{F}_3\text{B}\cdot\text{PH}_3$. In fact, we will show that our conclusion is fully consistent with all experimental observations.

5.2. Computational Details

All calculations were performed using the Gaussian09¹³ program. Optimization and frequency calculations were carried out primarily using second order Møller-Plesset perturbation theory (MP2).¹⁴ Coupled-cluster calculations with included single and double excitations (CCSD)¹⁵ were also employed as a means of verifying the results from the MP2 calculations. The 6-311++G(d,p) basis set¹⁶⁻¹⁷ was used for all calculations. Both the MP2 and the CCSD frequency calculations were used to obtain the thermochemistry data, rotational constants, and dipole moments for all relevant molecules. Structural parameters of $\text{F}_3\text{B}\cdot\text{PH}_3$ and $\text{F}_2\text{B}-\text{PH}_2$ are given in Table 5-2, and Cartesian coordinates of all stationary structures are provided in the Appendix.

Table 5-2. Structural data of F₃B·PH₃ and F₂B–PH₂ at the levels MP2(full)/6-311++G(d,p) and CCSD(full)/6-311G++(d,p)

Molecule	Bond Length (Å)			Bond Angle (°)				Dihed. (°)
	B–P	B–F	P–H	F–B–P	B–P–H	H–P–H	F–B–F	H–P–B–F
MP2(full)								
PH ₃			1.409			94.4		
BF ₃		1.318						
DB, Stag., short, 1ss	2.286	1.354	1.400	100.7	117.9	99.9	116.6	180.0
DB, Stag., long, 1sl	3.064	1.321	1.406	92.4	121.2	95.5	119.8	180.0
DB, Ecl., 1e	3.078	1.321	1.407	92.3	121.3	95.5	119.8	0.0
HB, Stag., 2s	3.525	1.318	1.409	90.6	57.8	94.2	120.0	180.0
HB, Ecl., 2e	3.602	1.317	1.409	90.6	57.6	94.0	120.0	0.0
H ₂ PBF ₂ , M, 3a	1.917	1.328	1.407	121.3	95.3	97.0	117.1	44.1
H ₂ PBF ₂ , ITS, 3b	1.831	1.331	1.380	120.6	122.7	114.6	118.8	0.0
H ₂ PBF ₂ , RTS, 3c	1.947	1.326	1.412	122.9	91.6	93.3	116.4	46.7
		1.325		120.7				133.4
HF	0.916							
PH ₄ ⁺			1.390					
BF ₄ [−]		1.414						
CCSD(full)								
PH ₃			1.413			94.2		
BF ₃		1.314						
DB, Stag., long, 1sl	3.107	1.316	1.411	92.1	121.3	95.4	119.9	180.0
DB, Ecl., 1e	3.114	1.317	1.411	92.0	121.4	95.3	119.9	0.0
HB, Stag., 2s	3.567	1.313	1.414	90.5	57.6	94.0	120.0	180.0
HB, Ecl., 2e	3.607	1.313	1.414	90.4	58.2	93.8	120.0	0.0
H ₂ PBF ₂ , M, 3a	1.924	1.324	1.411	121.4	95.3	96.8	116.9	44.1
H ₂ PBF ₂ , ITS, 3b	1.834	1.327	1.382	120.7	122.7	114.6	118.6	0.0
H ₂ PBF ₂ , RTS, 3c	1.953	1.323	1.417	122.9	92.0	93.3	116.3	46.7
		1.322		120.8				133.3
HF	0.914							
PH ₄ ⁺			1.392					
BF ₄ [−]		1.410						

Total energies and thermochemical parameters also are provided in the Appendix in Table 5- S1 (MP2) and Table 5- S2 (CCSD). Relative energies and reaction energies are listed in Table 5-3. Thermochemical analyses were performed for standard conditions (298.15 K) and also for the temperatures 203.15 K (-70 °C) and 143.15 K (-130 °C) and the data for the lower temperatures are presented in Table 5-8 (Appendix). A distinction between the thermochemistry of the gas phase molecules and that of the molecules in condensed/solution phase is necessary.

The internal energy, U , of a system is the sum of the total energy of the stationary structure, E_{tot} , and the thermal energy, TE , of the system. The thermal energy can be further divided into its components from translational, rotational, and vibrational motion. The total entropy, S , of a system is the sum of the entropies associated with translation, vibration, and rotation. For a given temperature, T , the Helmholtz free energy, A , is defined as $A = U - TS$. To obtain the Gibbs free energy, G , a volume term pV must be included in the manner: $G = U - TS + pV$. Using the definition of enthalpy, $H = U + pV$, one arrives at the more familiar formulation of the Gibbs free energy, $G = H - TS$. For an ideal gas ($R = 1.986 \text{ cal/mol K}$) at room temperature, the pV term equates to 0.592 kcal/mol.

For gas phase reactions, volume changes can be very large and therefore have a significant contribution to the reaction energy. In such cases, ΔG is obviously the best estimate of the spontaneity of reaction. However, in condensed/solution phase, the volume changes are largely diminished. Here, using the Gibbs free energy to judge reaction spontaneity is unrealistic because the effect of the volume change would be so greatly overestimated. Therefore, omission of the pV when judging spontaneity is warranted, i.e. the Helmholtz free energy is a better estimate of the spontaneity of reaction for condensed/solution phase reactions.

Table 5-3. Relative Energies of the F₃B·PH₃ and F₂B–PH₂ stationary structures.

Parameter	ΔE	ΔH_{298}	ΔG_{298}	$\Delta^w A_{298}$	ΔG_{203}	$\Delta^w A_{203}$	ΔG_{143}	$\Delta^w A_{143}$
MP2(full)/6-311++G(d,p)								
$E_{\text{rel}}, \mathbf{1ss} \text{ vs. } \mathbf{1sl}$	0.98	0.96	3.64	3.64	2.79	2.79	2.28	2.28
$E_{\text{act}}, \mathbf{1e} \text{ vs. } \mathbf{1sl}$	0.05	-0.54	1.36	1.37	0.84	0.84	0.51	0.51
$E_{\text{act}}, \mathbf{2e} \text{ vs. } \mathbf{2s}$	0.19	-0.44	0.60	0.60	0.35	0.35	0.19	0.19
$E_{\text{rel}}, \mathbf{2s} \text{ vs. } \mathbf{1sl}$	2.16	2.16	1.90	1.90	1.98	1.98	2.03	2.03
$E_{\text{rxn}}(\mathbf{1sl}), \text{BF}_3 + \text{PH}_3 \rightarrow \mathbf{1sl}$	-4.36	-3.15	3.05	0.76	0.73	-0.65	-0.56	-1.41
$E_{\text{rxn}}(\mathbf{2s}), \text{BF}_3 + \text{PH}_3 \rightarrow \mathbf{2s}$	-2.21	-0.98	4.95	2.66	2.71	1.33	1.48	0.62
$E_{\text{act}}, \mathbf{3b} \text{ vs. } \mathbf{3a}$, inversion	18.21	17.51	18.39	18.39	18.19	18.19	18.04	18.04
$E_{\text{act}}, \mathbf{3c} \text{ vs. } \mathbf{3a}$, rotation	3.97	3.23	3.97	3.97	3.83	3.83	3.73	3.73
$E_{\text{rxn}}, \mathbf{1sl} \rightarrow \mathbf{3a} + \text{HF}$	30.65	30.08	23.33	25.48	25.71	26.99	27.03	27.82
$E_{\text{rxn}}, \mathbf{1sl} + \text{HF} \rightarrow \text{BF}_4^- + \text{PH}_4^+$	101.15	100.95	104.90	105.06	103.74	103.85	103.12	103.20
$E_{\text{rxn}}, 2 \cdot \mathbf{1sl} \rightarrow \mathbf{3a} + \text{BF}_4^- + \text{PH}_4^+$	131.80	131.03	128.24	130.54	129.45	130.84	130.14	131.01
CCSD(full)/6-311++G(d,p)								
	ΔE	ΔH_{298}	ΔG_{298}	$\Delta^w G_{298}$				
$E_{\text{act}}, \mathbf{1e} \text{ vs. } \mathbf{1sl}$	0.04	-0.55	1.45	1.44				
$E_{\text{act}}, \mathbf{2e} \text{ vs. } \mathbf{2s}$	0.19	-0.44	0.60	0.60				
$E_{\text{rel}}, \mathbf{2s} \text{ vs. } \mathbf{1sl}$	2.09	2.07	1.82	1.82				
$E_{\text{b}}(\mathbf{1sl}), \text{BF}_3 + \text{PH}_3 \rightarrow \mathbf{1sl}$	-4.24	-2.89	3.22	0.82				
$E_{\text{b}}(\mathbf{2s}), \text{BF}_3 + \text{PH}_3 \rightarrow \mathbf{2s}$	-2.15	-0.82	5.04	2.64				
$E_{\text{act}}, \mathbf{3b} \text{ vs. } \mathbf{3a}$, inversion	19.38	18.69	19.58	19.58				
$E_{\text{act}}, \mathbf{3c} \text{ vs. } \mathbf{3a}$, rotation	3.73	2.99	3.74	3.74				
$E_{\text{rxn}}, \mathbf{1sl} \rightarrow \mathbf{3a} + \text{HF}$	31.47	30.98	24.32	26.46				
$E_{\text{rxn}}, \mathbf{1sl} + \text{HF} \rightarrow \text{BF}_4^- + \text{PH}_4^+$	102.10	101.85	105.93	106.10				
$E_{\text{rxn}}, 2 \cdot \mathbf{1sl} \rightarrow \mathbf{3a} + \text{BF}_4^- + \text{PH}_4^+$	133.57	132.83	130.24	132.56				

(a) ΔE in kcal/mol (b) ΔH_0 in kcal/mol (c) ΔH_{298} in kcal/mol (d) ΔG_{298} in kcal/mol (e) ΔH_{203} in kcal/mol (f) ΔG_{203} in kcal/mol

5.3. Results and Discussion

PES Analysis of $\text{H}_3\text{P}\cdot\text{BF}_3$ Complexes: Dative Bonding and Hydrogen Bonding

We studied the potential energy surface of the aggregate $\text{F}_3\text{B}\cdot\text{PH}_3$ as a function of the BP distance at the MP2(full)/6-311++G(d,p) and CCSD(full)/6-311++G(d,p) levels for the dative bonding complex **1** and the hydrogen-bonded complex **2** in the staggered (**s**) and eclipsed (**e**) conformations. The PES scans are shown in Figure 5-1 and molecular models of the MP2 stationary structures are shown in Figure 5-2.

Figure 5-1. Scans of the potential energy surfaces of F_3BPH_3 as a function of the BP distance at MP2(full)/6-311++G(d,p) and CCSD(full)/6-311++G(d,p), respectively. Solid lines indicate dative bonding complexes $\text{F}_3\text{B}\leftarrow\text{PH}_3$, **1** and dashed lines indicate H-bonded complexes $\text{BF}_3\cdots\text{H}_3\text{P}$, **2**. Line color and marker type indicate conformation (dark red, squares: staggered; dark blue, triangles: eclipsed), and larger, green circles indicate the locations of stationary structures. All energies are in kcal/mol and relative to infinitely dissociated BF_3 and PH_3 .

At the MP2 level, we located two staggered structures of **1s**: a very shallow local minimum **1ss** with a short bond length of $d(\text{B}-\text{P}) \approx 2.4$ Å and the much preferred van-der Waals complex **1sl** with the longer bond length $d(\text{B}-\text{P}) \approx 3.1$ Å. The eclipsed structure **1e** is slightly less stable and formally the transition state structure for rotation about the BP bond. The hydrogen bonded

structures **2** are less stable than the dative bonded structures **1**. The shallow local minimum **1ss** disappears at the CCSD level and all other features of the potential energy surfaces are quantitatively very similar at both levels. The structures of BF_3 and PH_3 are essentially retained in the van der Waals complexes (Figure 5-2 and Table 5-2).

Figure 5-2. Optimized structures of LALB-complex $\text{F}_3\text{B} \leftarrow \text{PH}_3$ (top), HB-complex $\text{BF}_3 \cdot \text{H}_3\text{P}$ (center), and $\text{F}_2\text{B}-\text{PH}_2$ (bottom). The MP2(full)/6-311++G(d,p) structures are shown. Values of $d(\text{H} \cdots \text{F})$ distances ($\text{\AA}$): $3.057\text{ \AA}$ (**2s**); $2.863\text{ \AA}$ (**2e**).

We also studied the thermochemistry of these systems at several temperatures, and the results are very clear: The complex $\text{F}_3\text{B} \cdot \text{PH}_3$ does not exist in the gas phase. The association of F_3B with PH_3 lowers the energy of the system but internal motions reduce the exothermicity of the

association reactions and the loss of molecular entropy renders the aggregation endergonic in the gas phase, $\Delta G_{298} = +3.05$ kcal/mol (CCSD). Lower temperatures reduce the entropy penalty significantly such that at very low temperatures, the aggregation becomes exergonic, which is shown by the values $\Delta G_{203} = +0.73$ kcal/mol and $\Delta G_{143} = -0.56$ kcal/mol (CCSD).

Does the $\text{H}_3\text{P}\cdot\text{BF}_3$ Complex exist in Condensed Phase? Entropy is Key

The complex $\text{F}_3\text{B}\cdot\text{PH}_3$ might still exist in condensed phase. While it is generally agreed that vibrational and rotational contributions to molecular entropy are about the same in the gas phase and in condensed phase, it is well known that the translational entropy S_{tr} in condensed phase is smaller than in the gas phase.¹⁸⁻²¹ We employed the Wertz equation²² to estimate the difference. With these more appropriate molecular entropies, we find that the association reaction of BF_3 and PH_3 is very slightly exergonic at -130°C with $\Delta^{\text{W}}A_{143} = -1.41$ kcal/mol and even at -70°C with $\Delta^{\text{W}}A_{203} = -0.65$ kcal/mol. This theoretical finding is highly significant because it shows that vibrational spectra can be measured for the complex in condensed phase at low temperature.

Structure, Formation, and Properties of Difluoroborylphosphane $\text{F}_2\text{B}-\text{PH}_2$

Since the $\text{H}_3\text{P}\cdot\text{BF}_3$ complex does not exist in the gas phase, the most pertinent question concerns the identity of the species that actually was observed experimentally via microwave spectroscopy. We argue that the published rotational constants show that the microwave study actually measured $\text{H}_2\text{P}-\text{BF}_2$.

Structure and Rotational Constants. The most stable difluoroborylphosphane structure **3a** contains a pyramidal phosphorus atom and the geometry at boron is essentially trigonal planar (Figure 5-2). The C_s -structure **3b** is the transition state structure for inversion at the phosphorus

atom with an activation barrier of $\Delta G = 19.6$ kcal/mol at room temperature. The $d(\text{P-B})$ distances in 3a – 3c are 1.924 Å, 1.834 Å, and 1.953 Å, respectively.

Table 5-4. Rotational constants and dipole moments of calculated structure for $\text{H}_3\text{P}\cdot\text{BF}_3$ and $\text{H}_2\text{P}\cdot\text{BF}_2$ complex as well as their isotopomers for comparison with experimental results (ref.6).

System	Rotational Constant (GHz)			Dipole
	A	B	C	
Experimental				
H ₃ P(¹¹ B)F ₃ in ref. 6			2.88932	3.73±0.3
H ₃ P (¹⁰ B)F ₃ in ref. 6			2.89235	
D ₃ P(¹¹ B)F ₃ in ref. 6			2.65414	
D ₃ P(¹⁰ B)F ₃ in ref. 6			2.65771	
MP2(fu)/6-311++G(d,p)				
DB, Stag., short, 1ss	4.79246	2.49479	2.49479	4.96
H ₃ P(¹¹ B)F ₃ , 1sl	4.87440	1.79340	1.79340	1.73
H ₃ P(¹⁰ B)F ₃	4.87440	1.79998	1.79998	
D ₃ P(¹¹ B)F ₃	4.67752	1.64799	1.64799	
D ₃ P(¹⁰ B)F ₃	4.67752	1.65446	1.65446	
DB, Stag. (ref. 10)	4.869	1.783	1.783	1.73
DB, Ecl., 1e	4.87485	1.78234	1.78234	
HB, Stag., 2s	4.89497	1.55074	1.55074	
HB, Ecl., 2e	4.89497	1.49441	1.49441	
H ₂ P(¹¹ B)F ₂ , 3a	9.61537	4.03195	2.89273	1.49
H ₂ P(¹⁰ B)F ₂	9.61548	4.03866	2.89618	
D ₂ P(¹¹ B)F ₂	8.99730	3.82820	2.77323	
D ₂ P(¹⁰ B)F ₂	8.99734	3.83532	2.77697	
CCSD(fu)/6-311++G(d,p)				
DB, Stag., 1sl	4.90418	1.76207	1.76207	1.49
DB, Ecl., 1e	4.90440	1.75550	1.75550	
HB, Stag., 2s	4.92091	1.54163	1.54163	
HB, Ecl., 2e	4.92278	1.48335	1.48335	
H ₂ P(¹¹ B)F ₂	9.67324	4.01066	2.88741	1.34
H ₂ P(¹⁰ B)F ₂	9.67333	4.01739	2.89089	
D ₂ P(¹¹ B)F ₂	9.04464	3.80790	2.76787	
D ₂ P(¹⁰ B)F ₂	9.04467	3.81503	2.77163	

The rotational constants for difluoroborylphosphane and its isotopomers are listed in Table 5-4 along with the published values observed the microwave spectrum that were thought to describe the $\text{H}_3\text{P}\cdot\text{BF}_3$ complex. The experimentally observed rotational constants for the “ $\text{F}_3\text{B}\cdot\text{PH}_3$ ” complex with the ^1H and ^{11}B isotopes were in excellent agreement with the $\text{H}_2\text{P}\cdot\text{BF}_2$

computational data. Slightly larger deviations arise for the deuterated complexes, but agreement is still very good between the **3a** isotopomers and the experimental data. However, the computed rotational constants for the most stable structure of the $F_3B \cdot PH_3$ complex, **1sl**, are much lower and do not fit the experimental data.

Rotational Barrier. The internal barrier to rotation calculated using the torsional excited state observed in the microwave spectrum was of 3.34 ± 0.35 kcal/mol.⁶ The internal barrier to rotation for H_2P-BF_2 calculated at MP2 is $\Delta G = 3.97$ kcal/mol and at CCSD level $\Delta G = 3.74$ kcal/mol. Again, these data are in fairly good agreement with the experimental data. The rotational barrier calculated for the $F_3B \cdot PH_3$ dative bonded complex was $\Delta G = 1.36$ kcal/mol, and does not match the experimental results.

Dipole Moment. The dipole moment for difluoroborylphosphane, **3a**, was calculated to be 1.34 D. The dipole moment for the dative bonded complex **1sl** was found to be 1.73 D. Both values are in contrast with the dipole moment calculated from the microwave spectrum, 3.73 ± 0.3 D.⁶ It is possible that the experimental determination of the dipole moment is incorrect and the assumption of a C_{3v} symmetry may be a reason for this discrepancy.²³

Vibrational Analysis. The calculated and experimental⁵ vibrational frequencies are listed in Table 5-5 at various levels of calculation. The first three columns list the frequencies for **1sl**, the long dative bonded $F_3B \cdots PH_3$ structure at MP2, CCSD, and then at MP2 as reported in ref. 11. The fourth column give the vibrational frequencies for **1ss**, the short dative bonded structure that is only identified as a minimum in the MP2 calculations. The fifth column lists the assignments of the frequencies listed. For a direct comparison of the VDW structures and the difluoroborylphosphane, the sixth and seventh columns list the vibrational frequencies of **3a** at MP2 and their assignments, respectively. The final two columns give experimentally determined

frequencies and the assignments reported in the literature.⁵ There are discrepancies between experiment and all of the computational structures; the higher frequencies of the measured data seem to track fairly well with both the $\text{F}_3\text{B}\cdots\text{PH}_3$ and the $\text{F}_2\text{B}-\text{PH}_2$ calculations but the lower frequencies seem to match more closely with the $\text{F}_2\text{B}-\text{PH}_2$ data. The IR and Raman spectra were examined individually and appear in the Appendix, and the peak intensities were compared to the experimental spectra. The experimentally measured IR spectrum is more similar to the calculated IR spectrum of $\text{F}_2\text{B}-\text{PH}_2$ in both the positions and the intensities of the peaks. However, the experimental spectrum was measured in the solid phase at low temperature so the spectral lines are much broader. The comparison of the calculated Raman spectra with the measured spectrum is inconclusive.

Table 5-5. Comparison of Calculated Frequencies to the Experimental Vibrational Spectra

Computation							Experiment	
1sl, MP2	1sl, CCSD	1sl, MP2 ¹¹	1ss, MP2	Assignment	3a, MP2	Assignment	Freqs. ⁵	Assignment
2540.7 ^a	2490.9	2538	2590.5	$\Gamma_{\text{PH,as}}$	2536.0	$\Gamma_{\text{PH,as}}$	2468	v7: Γ_{PH}
2529.1	2483.7	2527	2568.7	$\Gamma_{\text{PH,s}}$	2523.2	$\Gamma_{\text{PH,s}}$	2441	v1: Γ_{PH}
1417.3 ^a	1439.6	1416	1274.8	$\Gamma_{\text{BF}}, \delta_{\text{PH}}$	1348.1	$\Gamma_{\text{BF}}, \rho_{\text{PH}}$	1120	v8: $\Gamma_{\text{BF}}, \delta_{\text{PH}}, \delta_{\text{BF}}$
1160.0 ^a	1150.4	1161	1167.2	δ_{PH}	1229.3	$\delta_{\text{PH}}, \Gamma_{\text{PB}}$	1085	v9: $\delta_{\text{PH}}, \Gamma_{\text{BF}}$
1054.0	1061.0	1055	1054.1	$\delta_{\text{PH}}, \delta_{\text{BF}}$	1135.3	$\delta_{\text{PH}}, \Gamma_{\text{PB}}$	1021	v2: $\delta_{\text{PH}}, \Gamma_{\text{PB}}$
861.5	874.2	861	798.3	$\Gamma_{\text{BF,s}}, \delta_{\text{PH}}$	783.1	ρ_{PH}	797	v3: $\Gamma_{\text{BF}}, \Gamma_{\text{PB}}, \delta_{\text{BF}}$
628.2	645.6	627	562.0	$\delta_{\text{BF}}, \delta_{\text{PH}}$	740.0	$\delta_{\text{PH}}, \rho_{\text{BF}}$	607	v4: $\Gamma_{\text{PB}}, \delta_{\text{BF}}$
472.1 ^a	477.5	471	485.3	$\delta_{\text{BF}}, \rho_{\text{BF}}, \rho_{\text{PH}}$	639.7	$\Gamma_{\text{PB}}, \Gamma_{\text{BF,s}}$	570	v10: $\rho_{\text{PH}}, \delta_{\text{PH}}, \Gamma_{\text{BF}}$
190.7 ^a	186.5	190	381.6	$\rho_{\text{PH}}, [\rho_{\text{PH}}, \delta_{\text{BF}}]$	461.3	$\rho_{\text{PH}}, \rho_{\text{BF}}$	430	v11: δ_{BF}
75.5	79.3	75	146.9	$\Gamma_{\text{PB}}, [\rho_{\text{BF}}, \rho_{\text{PH}}]$	390.2	$\delta_{\text{BF}}, \Gamma_{\text{PB}}$	331	v5: $\delta_{\text{BF}}, \Gamma_{\text{PB}}, \Gamma_{\text{BF}}$
73.0 ^a	73.1	72	105.0	$\rho_{\text{BF}}, \rho_{\text{PH}}, [\Gamma_{\text{BP}}]$	251.6	ρ_{PB}	225	v12: $\rho_{\text{BF}}, \delta_{\text{BF}}, \Gamma_{\text{BF}}$
22.6	18.8	21	90.4	τ_{BP}	178.1	τ_{BP}		v6: unassigned

^a Frequencies are doubly degenerate.r: bond stretching, δ : deformation, ρ : rock, τ : torsion, s: symmetric, as: asymmetric

5.4. Conclusion

The measured microwave spectrum previously attributed to $F_3B\cdots PH_3$ actually corresponds to F_2B-PH_2 . The experimental measurements of the rotational constants agree much better with the results of the electronic structure calculations for the difluoroborylphosphane than for the dative bonded complex. The measured vibrational spectra are not inconsistent with the F_2B-PH_2 structure, but inconclusive with respect to whether they correspond to F_2B-PH_2 or $F_3B\cdots PH_3$. The thermochemistry results suggest that the $F_3B\cdots PH_3$ complex can exist in condensed phase at low temperatures, which is consistent with the vibrational studies, but the computed vibrational spectrum is not a clear match to the experimentally measured one. An updated measurement of the vibrational spectrum would be desirable. Further study will focus on the thermochemistry of reaction and re-generation and assignment of the microwave spectrum.

5.5. References

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5.6. Appendix

Table 5-6. Energies of the $F_3B \cdot PH_3$ and F_2B-PH_2 Stationary Structures Calculated at MP2(full)/6-311++G(d,p)

System	E_{tot}	VZPE	TE ₂₉₈	S_{298}	$^wS_{298}$	v_1	μ
MP2(full)							
PH ₃	-342.737649	15.62	17.44	50.14	39.93	1048.6	0.8081
BF ₃	-324.058654	7.71	9.91	60.86	49.70	475.5	0.0
DB, Stag., short, 1ss	-666.801699	24.69	29.14	81.23	69.51	90.4	4.9597
DB, Stag., long, 1sl	-666.803258	24.13	29.16	90.23	78.51	22.6	1.7367
DB, Ecl., 1e	-666.803176	24.10	28.57	83.84	72.12	-23.7	1.7113
HB, Stag., 2s	-666.799818	24.03	29.16	91.11	79.39	46.4	0.4220
HB, Ecl., 2e	-666.799511	23.85	28.53	87.62	75.90	-52.3	0.4876
F ₂ BPH ₂ , M, 3a	-566.456477	17.46	20.51	71.40	59.98	178.1	1.4915
F ₂ BPH ₂ , ITS, 3b	-566.427458	16.98	19.81	68.44	57.02	-723.8	2.3551
F ₂ BPH ₂ , RTS, 3c	-566.450145	17.12	19.77	68.94	57.52	-145.2	1.2418
HF	-100.297937	6.01	7.49	41.46	31.97	4201.3	2.0653
PH ₄ ⁺	-343.052887	23.03	24.89	51.24	40.99	1043.1	0.0
BF ₄ ⁻	-423.887114	8.80	11.56	67.21	55.71	347.9	0.0

Table 5-7. Energies of the F₃B·PH₃ and F₂B–PH₂ Stationary Structures Calculated at CCSD(full)/6-311G++(d,p)

System	E_{tot}	VZPE	TE ₂₉₈	S_{298}	ν_1	μ
PH ₃	-342.763741	15.36	17.19	50.17	1050.2	0.7115
BF ₃	-324.059691	7.81	10.00	60.80	480.6	0.0
DB, Staggered, 1sl	-666.830189	24.01	29.04	90.54	18.8	1.4937
DB, Eclipsed, 1e	-666.830120	23.98	28.45	83.86	-25.9	1.4843
HB, Staggered, 2s	-666.826866	23.89	29.02	91.37	45.5	0.2585
HB, Eclipsed, 2e	-666.826565	23.70	28.39	88.05	-51.2	0.3346
F ₂ BPH ₂ , M, 3a	-566.480164	17.39	20.44	71.44	172.3	1.3385
F ₂ BPH ₂ , ITS, 3b	-566.449277	16.91	19.74	68.44	-735.2	2.2545
F ₂ BPH ₂ , RTS, 3c	-566.474220	17.05	19.70	68.93	-140.1	1.0789
HF	-100.299877	6.04	7.52	41.45	4225.9	1.9541
PH ₄ ⁺	-343.080389	22.76	24.63	51.26	1033.3	0.0
BF ₄ ⁻	-423.886972	8.95	11.69	67.07	352.5	0.0

(a) E_{tot} in Hartrees. (b) VZPE in kcal/mol (c) TE in kcal/mol (d) S in cal/mol K (e) ν in cm⁻¹ (f) μ in Debye

Table 5-8. Thermochemistry of the F₃B·PH₃ and F₂B–PH₂ Stationary Structures Calculated at MP2(full)/6-311G++(d,p)

System	TE ₂₉₈	S ₂₉₈	^w S ₂₉₈	TE ₂₀₃	S ₂₀₃	^w S ₂₀₃	TE ₁₄₃	S ₁₄₃	^w S ₁₄₃
MP2(full)									
PH ₃	17.44	50.14	39.93	15.16	46.96	37.62	14.80	44.14	35.60
BF ₃	9.91	60.86	49.70	8.26	56.89	46.60	7.78	53.42	43.94
DB, Stag., short, 1ss	29.14	81.23	69.51	24.71	74.19	63.35	23.64	67.29	57.25
DB, Stag., long, 1sl	29.16	90.23	78.51	24.67	82.97	72.13	23.51	75.52	65.48
DB, Ecl., 1e	28.57	83.84	72.12	24.27	77.11	66.27	23.23	70.36	60.31
HB, Stag., 2s	29.16	91.11	79.39	24.67	83.84	72.99	23.50	76.32	66.27
HB, Ecl., 2e	28.53	87.62	75.90	24.23	80.86	70.01	23.17	73.98	63.94
F ₂ BPH ₂ , M, 3a	20.51	71.40	59.98	17.41	66.12	55.58	16.70	61.28	51.53
F ₂ BPH ₂ , ITS, 3b	19.81	68.44	57.02	16.84	63.40	52.86	16.18	58.88	49.13
F ₂ BPH ₂ , RTS, 3c	19.77	68.94	57.52	16.87	64.17	53.63	16.26	59.96	50.22
HF	7.49	41.46	31.97	6.37	38.79	30.18	6.07	36.36	28.55
PH ₄ ⁺	24.89	51.24	40.99	21.79	47.94	38.57	21.42	45.09	36.51
BF ₄ ⁻	11.56	67.21	55.71	9.48	62.18	51.56	8.84	57.77	47.94

Figure 5-3. Calculated IR and Raman spectra of F₂B-PH₂

Figure 5-4. Calculated IR and Raman spectra of $\text{F}_3\text{B}\cdots\text{PH}_3$.

F₃B...PH₃ Structures

1ss, DB staggered short BF₃·PH₃, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-0.726114
2	15	0	0.000000	0.000000	1.560100
3	9	0	0.000000	1.330062	-0.978428
4	9	0	1.151868	-0.665031	-0.978428
5	9	0	-1.151868	-0.665031	-0.978428
6	1	0	0.000000	-1.236757	2.215538
7	1	0	1.071063	0.618379	2.215538
8	1	0	-1.071063	0.618379	2.215538

1sl, DB staggered long BF₃·PH₃, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-1.117176
2	15	0	0.000000	0.000000	1.946808
3	9	0	0.000000	1.320007	-1.172049
4	9	0	1.143159	-0.660003	-1.172049
5	9	0	-1.143159	-0.660003	-1.172049
6	1	0	0.000000	-1.202336	2.676356
7	1	0	1.041254	0.601168	2.676356
8	1	0	-1.041254	0.601168	2.676356

1sl, DB staggered long BF₃·PH₃, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-1.136091
2	15	0	0.000000	0.000000	1.969664
3	9	0	0.000000	1.315723	-1.184353
4	9	0	1.139450	-0.657862	-1.184353
5	9	0	-1.139450	-0.657862	-1.184353
6	1	0	0.000000	-1.204264	2.704342
7	1	0	1.042923	0.602132	2.704342
8	1	0	-1.042923	0.602132	2.704342

1e, DB eclipsed BF₃·PH₃, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-1.123782
2	15	0	0.000000	0.000000	1.954489
3	9	0	0.000000	1.319955	-1.176032
4	9	0	1.143115	-0.659978	-1.176032
5	9	0	-1.143115	-0.659978	-1.176032
6	1	0	-1.041034	-0.601041	2.684812
7	1	0	1.041034	-0.601041	2.684812
8	1	0	0.000000	1.202083	2.684812

1e, DB eclipsed BF₃·PH₃, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-1.140173
2	15	0	0.000000	0.000000	1.974336
3	9	0	0.000000	1.315697	-1.186753
4	9	0	1.139427	-0.657849	-1.186753
5	9	0	-1.139427	-0.657849	-1.186753
6	1	0	-1.042824	-0.602075	2.709381
7	1	0	1.042824	-0.602075	2.709381
8	1	0	0.000000	1.204149	2.709381

2s, HB staggered BF₃·PH₃, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	0.000000	0.000000	2.307847
2	5	0	0.000000	0.000000	-1.216671
3	9	0	0.000000	1.317910	-1.229698
4	9	0	1.141344	-0.658955	-1.229698
5	9	0	-1.141344	-0.658955	-1.229698
6	1	0	0.000000	-1.191935	1.555833
7	1	0	1.032246	0.595967	1.555833
8	1	0	-1.032246	0.595967	1.555833

2s, HB staggered BF₃·PH₃, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	0.000000	0.000000	2.317307
2	5	0	0.000000	0.000000	-1.222466
3	9	0	0.000000	1.313854	-1.234436
4	9	0	1.137831	-0.656927	-1.234436
5	9	0	-1.137831	-0.656927	-1.234436
6	1	0	0.000000	-1.194583	1.560836
7	1	0	1.034539	0.597292	1.560836
8	1	0	-1.034539	0.597292	1.560836

2e, HB eclipsed BF₃·PH₃, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	0.000000	0.000000	2.357689
2	5	0	0.000000	0.000000	-1.243953
3	9	0	0.000000	1.317701	-1.257542
4	9	0	1.141162	-0.658850	-1.257542
5	9	0	-1.141162	-0.658850	-1.257542
6	1	0	-1.030600	-0.595017	1.602686
7	1	0	1.030600	-0.595017	1.602686
8	1	0	0.000000	1.190034	1.602686

2e, HB eclipsed BF₃·PH₃, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	0.000000	0.000000	2.369300
2	5	0	0.000000	0.000000	-1.251132
3	9	0	0.000000	1.313685	-1.263458
4	9	0	1.137684	-0.656842	-1.263458
5	9	0	-1.137684	-0.656842	-1.263458
6	1	0	-1.032889	-0.596338	1.609843
7	1	0	1.032889	-0.596338	1.609843
8	1	0	0.000000	1.192677	1.609843

F₂B–PH₂ Structures

3a, M, F₂B-PH₂, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.009000	-0.510980	0.000000
2	15	0	0.051310	1.406031	0.000000
3	9	0	0.051310	-1.202643	1.132396
4	9	0	0.051310	-1.202643	-1.132396
5	1	0	-0.869108	1.556005	-1.053501
6	1	0	-0.869108	1.556005	1.053501

3a, M, F₂B-PH₂, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.010796	-0.513866	0.000000
2	15	0	0.051305	1.409919	0.000000
3	9	0	0.051305	-1.205461	1.128491
4	9	0	0.051305	-1.205461	-1.128491
5	1	0	-0.873525	1.559421	-1.055065
6	1	0	-0.873525	1.559421	1.055065

3b, Inversion TS, F₂B-PH₂, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-0.510760
2	15	0	0.000000	0.000000	1.320463
3	9	0	0.000000	1.145803	-1.188111
4	1	0	0.000000	1.161340	2.066433
5	1	0	0.000000	-1.161340	2.066433
6	9	0	0.000000	-1.145803	-1.188111

3b, Inversion TS, F₂B-PH₂, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.000000	-0.511768
2	15	0	0.000000	0.000000	1.322266
3	9	0	0.000000	1.141343	-1.189612
4	1	0	0.000000	1.163211	2.068932
5	1	0	0.000000	-1.163211	2.068932
6	9	0	0.000000	-1.141343	-1.189612

3c, Rotational TS, F₂B-PH₂, MP2(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.517014	0.000000
2	15	0	-0.161326	-1.423266	0.000000
3	9	0	1.169854	1.141687	0.000000
4	9	0	-1.079054	1.286071	0.000000
5	1	0	0.801349	-1.542946	1.026789
6	1	0	0.801349	-1.542946	-1.026789

3c, Rotational TS, F₂B-PH₂, CCSD(full)/6-311++G(d,p)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	5	0	0.000000	0.520150	0.000000
2	15	0	-0.161940	-1.425630	0.000000
3	9	0	1.166834	1.143043	0.000000
4	9	0	-1.075083	1.289371	0.000000
5	1	0	0.801669	-1.554011	1.030561
6	1	0	0.801669	-1.554011	-1.030561

Statement of Collaboration

Multi-equilibria, Kinetics, and Oscillating Reactions: Video Colorimetry and Dynamical Approach to Mass Action

After joining the Glaser group in the Spring of 2015, I began working on the development of methods for solving systems of equations to determine kinetic parameters of multi-equilibria chemical systems, which we hoped to apply to oscillating reactions. Prior to my engagement with the project, a Mathematica script had been developed in collaboration with Dr. Carmen Chicone and Marco Downing to solve a system of differential equations to obtain equilibrium concentrations in multi-equilibria systems. The first paper from the dynamics group was published in *JCE* in 2014 and presented a comparison of the kinetic approach to the standard analytical approach.¹ I worked first with Marco and later with another undergraduate student, Ethan Zars to further develop these methods to solve multi-equilibria for more complicated systems and to account for non-ideal conditions by adding ionic strength considerations based on Debye-Hückel theory. This effort led to two full research publications, one in the *Journal of Solution Chemistry*² in 2017 and another in the *Journal of Chemical and Engineering Data*³ in 2018. I am the first author of the *JCED* publication and this work is included in the present dissertation as Chapter 4. This work was presented at the ACS Spring National Meeting in New Orleans in 2018.^a

The multi-equilibria work was the run-up to a much more ambitious project, namely the simulation of the kinetics of Belousov-Zhabotinsky (BZ) oscillating reactions based on actual reaction conditions and without any simplifying assumptions. We worked primarily on the classical cerium-catalyzed BZ reaction, on the popular ferroin-catalyzed BZ reaction, and on the so called “four color” BZR, the iron/cerium-catalyzed BZ reaction. The first challenge was the

development of a video-based method to measure the kinetics experimentally. Marco Downing laid the groundwork by writing Mathematica software that utilized the RGB data of the video images to determine “DCC” parameters to accurately measure timing information about the oscillation patterns. Ethan Zars studied the pH dependence of the iron-catalyzed reaction and the dynamic group’s first big break came with the mechanistic explanation of the pH dependence of the kinetics of this reaction.⁴ Excellent agreement between measurements and simulations required a modification to the commonly accepted FKN reaction scheme in the reduction of the catalyst. Together with Ethan, I wrote a book chapter that describes the video-based analysis of the four color reaction in detail.⁵

The next phase of the group’s work on oscillating chemical reactions began at Missouri S&T in the Fall of 2018. We recruited the outstanding undergraduate student, Sara McCauley, and started work to show that video-based analysis is capable of producing quantitative concentration data. What began as a study to verify video-based analysis by comparison to simultaneous UV-Vis measurements turned into a re-analysis and improvement of the video-based methods. The Vector Projection method was developed and we demonstrated that it is possible to simultaneously obtain timing *and* concentration information about various systems including oscillating reactions. The development of the new technique is described in Chapter 3 of this dissertation and has been recently accepted for publication.⁶ We presented this work at the 2019 ACS Regional Meeting in Wichita.^b

Biomimetic CO₂ Capture from Air: Ab initio Theory, ONIOM Methods, and Experimentation

Another major focus of my work as a graduate student has been concerned with studies of carbon dioxide capture from air, which will be an essential component to combat global climate change and restore acceptable atmospheric CO₂ levels over decades. Our approach mimics the carbon

dioxide capture in Rubisco, the enzyme responsible for carbon fixation in plants, and this research has been funded by NSF. The active site of Rubisco features the KDDE tetrapeptide which needs to be activated by lysine carbamylation. Our group focuses on the development of reversible CO₂ capture systems based on this activation reaction. The thermochemistry of a small model system was studied⁷ and has provided guidance to the project. The carbon dioxide sequestration research involved the simultaneous application of simulation, computation, and experimentation.

In the Fall of 2015, I worked with an undergraduate student, Andy Muelleman, to simulate the thermochemistry of the capture reaction and determine some ideal parameters for capture-and-release systems at various pressure conditions. The results from this study were published in 2016⁸ and guided the investigations into CO₂ capture systems in our group. In parallel, I performed *ab initio* studies of the thermochemistry of the capture reactions of ethyl-, propyl-, and butylamine. These studies focused on an examination of the effect of the populations of substrate and product conformations on the free energy of the capture. The results of this study are presented in Chapter 1 of this work, and the results were presented at the 2018 ACS Spring National in New Orleans^c and 2018 ACS Regional Meetings in Ames, Iowa.^d

For the experimental investigations, I worked closely with graduate student Kaidi Yang, and together, we analyzed the capture of CO₂ by aqueous butylamine with NMR techniques.

Butylamine is a good model system to approximate the lysine side chain in KDDE and the experimental results are presented in Chapter 2. We were able to use the butylamine NMR data to calculate the Gibbs free energy of the capture reaction for direct comparison to our theoretical work. We presented the findings of this study at the 2018 ACS National Meeting^c and then an update at the 2018 ACS Regional Meeting.^e

Upon successfully completion of the pilot study of the carbamylation of butylamine, we set out to perform analogous but much more challenging studies with the tetrapeptide, KDDE. This tetrapeptide was synthesized by Dr. Fabio Gallazzi, and we were assisted in the NMR measurements by Dr. Wei Wycoff. The results of the experimental carbamylation study are being written up. In parallel, we also investigated specific features of the mechanism of the capture of CO₂ by KDDE with theoretical methods, including possible reaction pathways, conformations, and protonation states. Kaidi Yang has been spearheading this work and a progress report was presented at the 2018 ACS Regional Meeting in Ames, Iowa.^f

We learned a lot about the Rubisco mechanism over the last few years. One of the most important insights was the realization that we would not be able to study the carbamylation reaction of KDDE at a pH where the KDDE is complexed by a magnesium ion. It is a characteristic trick of Rubisco to lower the pK_a of the ammonium ion of the lysine side chain so that sufficient free amine is available at physiological pH, a pH that allows Mg²⁺ ion complexation. This issue can be addressed by chemical modification of lysine in the KDDE model or by using a larger oligopeptide. The strategy of chemical modification of lysine is being pursued by graduate student Brian Jameson and undergraduate student Chris Dempsey with various fluorination concepts to depress the lysine pK_a .

We have been spending considerable efforts to understand this pK_a depression in Rubisco in the hope of modifying our oligopeptide model in a suitable fashion, and much of my work was focused on this exciting aspect. In the Fall of 2018, we recruited a very bright and dedicated undergraduate student at Missouri S&T, Kari Knobbe, to further explore the active site of Rubisco. More detailed studies of its structure shows that Rubisco achieves this goal by accumulating a high number of positively-charged histidine, lysine, and arginine residues in

proximity to the reactive lysine. Together, we worked to develop a large-scale model system of the enzyme that includes all residues in the vicinity of the active site and more precisely mimics the enzymatic situation. We have analyzed this model with ONIOM methods and we presented the preliminary results at the 2019 Regional ACS Meeting in Wichita.^g As a direct consequence of this investigation, we have now started experimental work on larger oligopeptides that include the KDDE sequence and additional positively-charged amino acids appended to the K residue.

The rubisco work required the application of the multilevel method, ONIOM. The Glaser group was already engaged in ONIOM studies on a different project, the cytochrome P450-catalyzed steroid oxidation. In the Fall of 2017, I started working with the undergraduate students Kaitlyn Chetney and Casey Hawkins on this project until their graduation in the spring of 2018. Work on this project resumed at Missouri S&T in the fall of 2018 and served as a starter project for Kari Knobbe. We developed a small model system to explore potential reaction mechanisms for the oxidation of deoxycorticosterone by the active site of the enzyme. Then, we used ONIOM methods to survey the potential energy surface in the larger enzyme environment and determine the feasibility of these mechanisms. This work will be presented at the upcoming 2020 ACS Fall National Meeting (planned for San Francisco, changed to virtual event because of COVID19).^h

Scholarship of Teaching and Mentoring

During my time at MU, I have had the pleasure of teaching chemistry courses for several semesters. I taught General Chemistry CHEM 1320 lab sections for many semesters (FS14, SP15, SS15, FS15, FS16) and thoroughly enjoyed working with the undergraduate students that were getting their first taste of chemistry at the college level. For three semesters (SP16, SP17, SP18), I served as the teaching assistant for the writing-intensive upper-level undergraduate chemistry seminar CHEM 3700 and, for the SP17 semester, the course was cross-listed to

include second-year graduate students as well, CHEM 7087. The seminar involved assignment-based instruction on all aspects of scientific writing and authoring. I particularly enjoyed teaching this course because it both fostered a very specific way of approaching scientific problems and truly engaged the students in the art of effective science communication. Part of the course involved an external science outreach event that, as the teaching assistant, I was in charge of coordinating. The goal, of course, was to showcase what the students had learned during the course about the semester-specific macroethical theme and to engage the students in effective science communication with the public. In the spring of 2016, the theme of the course was International Year of Pulses in which the students learned about phytochemicals prominent in pulses and their nutritional benefits. The science communication event that year was a Pulse Feast in which each student brought a pulse-based dish to share with classmates and their invited guests at lunch, all while discussing the chemistry of the pulses in each dish. In SP17, the theme was Carbon Capture, Utilization, and Storage (CCUS) in which the students looked at recent developments in CCUS methods and technologies. The science outreach event for that year was combined with a larger Science Festival in Columbia focused on the promotion of public engagement in science and the students maintained a booth at the Festival. For SP18, the theme was The Opioid Crisis and the students learned about different opioids and their effects on the body, as well as opioid inhibitors. For the scientific outreach event, I worked with co-Teaching Assistant, Kaidi Yang, to put together a lecture for a public audience that was given by Dr. Fred Rottnek, the lead Primary Care trainer for the Missouri Opioid State Targeted Response. These events were amazingly well received by the students and the public audience; they solidified the impact that the course had on the students' understanding of chemistry in context and former students routinely refer to these events as key experiences in their undergraduate careers.

In my last three years as a graduate student, I was supported by research assistantships and was able to focus all my efforts on research. Yet, the research effort also included a lot of education in the form of mentoring beginning graduate students and undergraduate students. With the group moving to Missouri S&T in the Fall of 2018, I was very much involved in building up a new lab and a new research group. Several bright undergraduate students joined the group within months and I was delighted to mentor most of them. I worked most closely with: Kari Knobbe, Sara McCauley, Gabriel Pleimann, Chris Dempsey, Stephen Murphy, Audrey Schuman, Christina Arens, and Henry Politte. It was an absolute pleasure to work with these students and provide supportive guidance to their projects. Each of these students has shown strong dedication and fierce intellectual fortitude and it will be interesting to see where these research experiences will take them.

Lastly, I want to mention that my dedication to promoting critical thinking does not stop in the classroom or in the lab. As a hobby, in 2019, I began to practice Street Epistemology (SE). SE is a conversational tool where a practitioner engages another person in conversation, usually in a public venue, and respectfully asks questions to challenge their beliefs (on any topic). The goal of SE is to help people to critically examine the reasons why they believe something to be true and, ultimately, to help people proportion their confidence in their beliefs appropriately with respect to their epistemological foundations. Now, perhaps more than ever before, it is vital that people are able to fully understand and interpret information critically and the practice of SE is an impactful and rewarding way to help individuals hone their critical thinking prowess.

Selected Presentations

- (a) Schell, J.; Zars, E.; Chicone, C. Glaser R. Toward quantitative H_2PO_4^- sensing: Simultaneous determination of all species concentrations in multiequilibria of aqueous solutions containing dihydrogen phosphate. Symposium on "Current State of Environmental Contamination Research: Theory & Experiment", Division of Environmental Chemistry, 255th ACS National Meeting, New Orleans, Louisiana, March 22, **2018**.
- (b) McCauley, S.; Schell, J.; Glaser, R. Expanding on Recent Colorimetry Methods to Include Multicomponent Systems Using Vector Analysis in the 3D RGB Color Space. Contributed Poster, Division of Analytical Chemistry, 2019 ACS Midwest Regional Meeting, Wichita State University, Wichita, KS, October 17, **2019**.
- (c) Yang, K.; Schell, J.; Glaser, R. Computational and experimental study of CO_2 capture by alkylamines. Contributed Lecture, Symposium on "Carbon Dioxide Conversion and Artificial Photosynthesis", Division of Energy and Fuels, 255th ACS National Meeting, New Orleans, Louisiana, March 19, **2018**.
- (d) Schell, J.; Glaser, R. E. Exploration of the conformational space of small alkylamines and alkylcarbamic acids in aqueous solution. Using a Boltzmann statistical analysis to improve the accuracy of the thermochemical data of the CO_2 capture reaction. Contributed Lecture, Symposium on "Chemistry from the Computer: Applications", 2018 ACS Midwest Regional Meeting, Iowa State University, Ames, IA, October 21-23, **2018**.
- (e) Schell, J.; Yang, K.; Wycoff, W.; Glaser, R. Determination of the thermochemistry of CO_2 capture by alkylamines in aqueous solution using NMR techniques and density functional theory. Symposium on "Carbon Capture, Utilization, and Storage", 2018 ACS Midwest Regional Meeting, Iowa State University, Ames, IA, October 21-23, **2018**.

- (f) Yang, K.; Schell, J.; Glaser, R. Computational study of CO₂ capture by the rubisco-inspired tetrapeptide KDDE. Symposium on "Carbon Capture, Utilization, and Storage", 2018 ACS Midwest Regional Meeting, Iowa State University, Ames, IA, October 21-23, **2018**.
- (g) Knobbe, K.; Schell, J.; Glaser, R. ONIOM Computational Study of the Thermochemistry of Activation and Carbamylation Reactions of Rubisco. Contributed Poster, Division of Physical Chemistry 2019 ACS Midwest Regional Meeting, Wichita State University, Wichita, KS, October 18, **2019**.
- (h) Knobbe, K.; Schell, J.; Glaser, R. Computational investigation of enzymatic steroid oxidation by cytochrome P450 (CYP11B2) using multilevel methods. Contributed Poster, Division of Physical Chemistry 2020 ACS Fall National Meeting, San Francisco, CA, August 17-20, **2020**.

Publications

- (1) Glaser, R. E.; Delarosa, M. A.; Salau, A. O.; Chicone, C. Dynamical Approach to Multi-Equilibria Problems for Mixtures of Acids and Their Conjugated Bases. *J. Chem. Ed.* **2014**, *91*, 1009-1016.
- (2) Zars, E.; Schell, J.; Delarosa, M.; Chicone, C.; Glaser, R. Dynamical Approach to Multi-Equilibria Problems Considering Debye-Hückel Theory of Electrolyte Solutions. Concentration Quotients as a Function of Ionic Strength. *J. Solution. Chem.* **2017**, *46*, 1-20.
- (3) Schell, J.; Zars, E. Chicone, C., and Glaser, R. Simultaneous Determination of All Species Concentrations in Multi-Equilibria for Aqueous Solutions of Dihydrogen Phosphate Considering Debye-Hückel Theory. *J. Chem. Eng. Data* **2018**, *63*, 2151-2161.

- (4) Zars, E.; Glaser, R. E.; Downing, M.; Chicone, C. Measurements and Simulations of the Acidity Dependence of the Kinetics of the Iron-Catalyzed Belousov-Zhabotinsky Reaction. Proton-Catalysis in the Electron Transfer Reaction Involving the $[\text{Fe}(\text{phen})_3]^{3+}$ Species *J. Phys. Chem. A* **2018**, *122*, 6183-6195.
- (5) Glaser, R. E.; Downing, M.; Zars, E.; Schell, J.; Chicone, C. Video-Based Kinetic Analysis of Period Variations and Oscillation Patterns in the Ce/Fe-Catalyzed Four-Color Belousov-Zhabotinsky Oscillating Reaction. Chapter 15 in *It's Just Math: Research on Students' Understanding of Chemistry and Mathematics*. Marcy H. Towns, Kinsey Bain, Jon-Marc G. Rodriguez, Eds. ACS Books, **2019**, pp. 251-270.
- (6) Schell, J.; McCauley, S. C.; Glaser, R. Video Colorimetry of Single-Chromophore Systems Based on Vector Analysis in the 3D Color Space: Unexpected Hysteresis Loops in Oscillating Chemical Reactions. *Talanta*, accepted (06/16/20).
- (7) Glaser, R.; Castello-Blindt, P. O. Yin, J. Biomimetic Approaches to Reversible CO₂ Capture From Air. N-Methylcarbaminic Acid Formation in Rubisco-Inspired Models. Chapter 17 in *New and Future Developments in Catalysis. Activation of Carbon Dioxide*. Steven L. Suib, Ed., 1st ed. Elsevier Publishers: **2013**, pp. 501-534.
- (8) Muelleman, A.; Schell, J.; Glazer, S.; Glaser, R. Thermochemistry of a Biomimetic and Rubisco-Inspired CO₂ Capture System from Air. *C – Journal of Carbon Research* **2016**, *2*, 18.

VITA

Joseph Schell was born on February 3, 1992, in Quincy, Illinois. He completed his primary and secondary education in Quincy, then moved to Saint Louis, Missouri, to study chemistry at Saint Louis University. He graduated from Saint Louis University in 2014 with his Bachelor of Science degree in Chemistry and a minor in Philosophy. Joseph started his graduate work at the University of Missouri-Columbia in the Fall of 2014. He proposed to his fiancée, Laci Le, in May of 2019, and is looking forward to many happy years together with her.