**CROSSED-BEAM CHEMICAL REACTION DYNAMICS
PROBED WITH UNIVERSAL AND STATE RESOLVED
ION IMAGING**

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In Partial Fulfillment

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DOCTOR OF PHILOSOPHY

By

ALEXANDER KAMASAH

Dr. Arthur G. Suits, Thesis Supervisor

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The undersigned, appointed by the Associate Vice Chancellor of the Office of Research and Graduate Studies, have examined the dissertation entitled

CROSSED-BEAM CHEMICAL REACTION DYNAMICS PROBED
WITH UNIVERSAL AND STATE RESOLVED ION IMAGING

presented by Alexander Kamasah,
a candidate for the degree of doctor of philosophy, Chemistry and hereby
certify that, in their opinion, it is worthy of acceptance.

Professor Arthur G. Suits

Professor Timothy Glass

Professor Michael Greenlief

Professor Aigen Li

DEDICATION

This dissertation is dedicated to

My Wife: Kamasah, Marian;

My Kids: Mich and Josh;

My parents of blessed memory:

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CHAPTER 1

INTRODUCTION

The main goal of chemical reaction dynamics is to unravel the intimate motions of individual atoms during a chemical transformation. This information must generally be inferred from indirect macroscopic measurement. Very important information such as translational energy dependence of the reaction cross-section, vibrational mode-specific promotion of reactivity, product angular and velocity distributions are normally extracted. Understanding how these chemical reactions occur at the microscopic level gives us a better insight in understanding reactive intermediates and products of reaction. For a better understanding of the elementary chemical reactions, it is imperative that the studies are performed under well-defined laboratory conditions. Over the last few decades, the field has witnessed unprecedented advances in both experiment and theory. Advancements in generating reactants, state selection, improvement of crossed-molecular beam machines and products detection have gone a long way to improve our ability in studying chemical reactions in the gas phase. In 1986, Hershbach,¹ Lee², and Polayni³ together shared the Nobel Prize in Chemistry for their work on the dynamics of gas phase reactions.

The study of bimolecular reactions using crossed-molecular beams continues to play pivotal role in understanding reaction dynamics. The single collision conditions of crossed molecular beam experiments permits the unambiguous identification of primary products which is very important in cases where very highly reactive species such as radicals are used as reactants or are formed as products. The experiment is performed by

crossing two collimated beams (a target beam and radical beam) normally at an angle of 90° , and the resulting products are scattered into different angles. The angle-resolved flux is known as the differential cross section (DCS)⁴ and is probed using different detection schemes such as resonance enhance multiphoton ionization (REMPI)⁵, laser induced fluorescence (LIF)⁶, or DC slice imaging⁷.

This technique provides us with the product velocity distribution, which tells us how much available energy has been partitioned into translational, rotation or internal excitation of the products. The product angular distribution, $I(\theta)$, in the center-of-mass frame gives us the details of the mechanism of the reactions and usually contains some information on the lifetime of the collision complex.

A crossed molecular beam experiment involves bimolecular collisions and these collisions result in scattering processes. Although in crossed-molecular beam experiments we do not have any way of controlling the impact parameter, we can control the relative velocities of the reactant species at specific energies. The same basic law that governs macroscopic collisions, for example, the laws of conservation of momentum and energy, usually governs molecular collisions. In most of these individual collisions, they are characterized by an impact parameter, b , the relative velocities of the colliding species v_{rel} , and the scattering angle θ . Scattering experiments are performed to obtain information on the forces between the colliding particles; In addition, measuring the cross section gives information on the part of interaction potential that is responsible for the energy transfer. Molecular collisions that result in scattering can be categorized into three main types: Elastic, inelastic, and reactive scattering. Elastic scattering is scattering in which translational energy is conserved. The collision partners have the same total

translational kinetic energy after the collision as they did before the collision and no energy is transferred into internal degrees of freedom. Inelastic scattering is scattering in which kinetic energy is not conserved, and energy is converted between different forms e.g. translational to rotational or vibrational. Inelastic scattering data provide direct information on both the attractive as well as repulsive parts of the intermolecular potentials. Rotational energy transfer is one of the simplest and important scattering processes in collision dynamics and can be described by

Where A is an atom, BC is a diatomic molecule, J is the rotational quantum number of the molecule, i and f are the initial and final states respectively, and ΔE is the change in translational energy.

Reactive scattering is a collision process that leads to a chemical change i.e. a collision in which chemical bonds are made or broken so that the species leaving the collision region are chemically distinct from those that entered.

When two molecules collide, the products are scattered in a variety of directions relative to the direction of approach. The scattered products can be described either in the laboratory or center of mass frame, and they are described in terms of scattering angle and the beam velocities. Although, the description of events in the laboratory frame of reference is always the first thing experimentalist look out for, it is more appropriate to describe the collisions in the center of mass frame. For example, in the laboratory frame it is difficult in comparing experimental results obtained for different parameters such as collision angle between two molecular beams. The use of center of mass frame under such scenarios gives experimentalist a better understanding of the collision dynamics. In

the center of mass frame collisions are characterized in terms of both relative velocities of the collision partners and center of mass frame. In crossed-molecular beam experiments, the angular distribution of the scattered product is contained in the Newton sphere whose center is the center of mass of the colliding species. We are able to tell the angular distribution of the scattered products by defining the products as either forward, sideways or backwards as illustrated in the example shown in figure 1.0. The figure illustrates the angular scattering distributions with the Newton diagram superimposed on it.

Figure 1.0 Center-of-mass distribution of the C_4H_7 radical from the reaction between C_4H_8 and HCl .

Lab frame measurements such as speed and angles can be transformed to the center of mass frame by using geometric relationship between the velocity vectors (Newton

diagram) which provides a kinematic analysis of the reaction as shown in Figure 1.1. In this figure, the velocities in the laboratory frame are represented by v_1 and v_2 while the relative velocities in the center of mass frame are u_1 and u_2 . The relation between the velocity vectors 1 and 2 in the center of mass and laboratory frame is expressed as

$$\mathbf{V}_{\text{CM}} = \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{M}$$

$$\mathbf{U}_1 = \frac{m_2}{M} \mathbf{v}_{\text{rel}}$$

$$\mathbf{U}_2 = \frac{m_1}{M} \mathbf{v}_{\text{rel}}$$

The relative velocity, $\mathbf{V}_{\text{rel}}$ is expressed as

$$\mathbf{V}_{\text{rel}} = \mathbf{u}_1 - \mathbf{u}_2 = \mathbf{v}_1 - \mathbf{v}_2$$

The angle between the relative velocity vectors, (θ) is center of mass scattering angle and the relation between the center of mass speed of the scattered products to their relative velocity is given by

$$\mathbf{U}_1 = \frac{m_2}{M} \mathbf{V}'_{\text{rel}}$$

$$\mathbf{U}_2 = -\frac{m_1}{M} \mathbf{V}'_{\text{rel}}$$

Figure 1.1. Newton diagram showing the relation between the laboratory and center of mass velocities. The laboratory frame is denoted by v and the center-of-mass frame is denoted by u . Θ and θ are the deflection angles in laboratory and center-of-mass frames respectively.

The use of DC slice imaging technique, described in chapter 2.4, has the advantage of directly providing the translational energy and the angular distribution without any inversion methods. The evolution of theoretical calculations have given us much more insight with the ability to explore the potential energy surface to give us better understanding of the reaction dynamics.

My dissertation discusses two main detection techniques in probing scattered products. The first section involves using state resolved detection to probe inelastic scattering of vibrationally excited NO ($v=1$) with Ar, and the second part involves using universal detection to probe reactive scattering of O(3P) with a series of target systems

(Amines and Alcohols). The outline of the thesis is structured as follows: Chapter 2 focuses on the experimental techniques used in these studies. An overview of crossed-molecular beam, ion imaging, universal detection, resonance enhanced multiphoton ionization (REMPI) will be discussed. The study of the collisions of NO ($X^2\Pi$) with Ar reactions has been the benchmark in studying rotational energy transfer. Chapter 3 of the thesis describes results of experiments using our crossed-beam DC slice ion imaging apparatus to image the inelastic scattering of vibrationally excited NO ($v=1$) with Ar. Chapter 4 of the thesis reports the use of single photon ionization to investigate the reaction dynamics of the reaction between O (3P) with Amines and the role of intersystem crossing on the singlet-triplet surface of the H- abstraction mechanism. Theoretical calculations are also carried out to get a better understanding of the reaction mechanism. Oxygenated systems such as alcohols for a very long time have been of great interest to experimentalists and theoreticians because of the very important roles they play in combustion and atmospheric chemistry. These systems offer special dynamical interest in understanding the mechanism of these reactions with O (3P). Chapter 5 deals with understanding the mechanism of H-atom abstraction of O (3P) radicals with n-propanol and iso-propanol using universal detection to probe the scattered hydroxyalkyl products. Collision energy dependence studies were performed for the two different types of alcohols under study.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Crossed Molecular Beams

Molecular beams are produced by allowing a gas at higher pressure to expand through a small orifice, and with the help of a skimmer are collimated into an evacuated chamber. This results in the production of a beam of particles (radicals, atoms, molecules or ions) moving with almost the same velocities and with few collisions occurring between them. Generally, the gas expansion is characterized by the Knudsen number which is expressed as $K_n = \lambda/d$, where λ is the mean free path of the molecules in the gas reservoir and d is the diameter of the nozzle. For $K_n \geq 1$, the molecules do not collide frequently in the nozzle vicinity and the molecular beam generated is termed an effusive beam. Effusive beams normally have low intensities that are insufficient for scattering experiments. This type of beam is characterized by a broad Maxwell-Boltzmann distribution. But if the Knudsen number satisfies $K_n \ll 1$, a supersonic condition can be achieved resulting in fast molecular beams with narrow velocity distributions, high density, and small angular divergence. If $\lambda \ll d$, many collisions occur during the expansion thereby establishing a local equilibrium at each point along the expansion and at this point it is treated as an adiabatic process. The molecules, which are accelerated by the pressure difference, reach the local sonic speed at the nozzle throat and then as the local temperature (and speed of sound) drops the term supersonic expansion becomes appropriate. The total energy available per molecule in the gas container is converted into kinetic energy and the rotational temperature of the beam becomes very close to the low

translational temperature. A typical free jet expansion is illustrated schematically in Fig.

2.0

In this way a stream of gas molecules can be directed towards a specific target. Molecular beams allow the study of a system that is far away from equilibrium due to the fact that the translational and internal energy of the molecules in the beam can be tuned independently. Atomic and molecular beams for decades have been very useful to experimentalists in probing chemical reactivity⁴⁻⁸ and molecular structures.⁹ One can vary both the conditions under which a molecular beam is formed and the composition of the gas mixture in order to have control of the most probable speed of the atoms, degree of clustering resulting from the expansion of the beam,¹⁰ and the effective temperature of the molecules in the beam.¹¹ By using a small amount of molecules of interest seeded in a light carrier gas, we are able to generate supersonic beams with very low rotational temperature thereby converting the enthalpy of the gas to bulk translational energy.¹² Very low gas density characterizes molecular beams hence the need to propagate them through a medium that does not disturb them over the length scale of the experiment. The mean free path of the propagation beam has to be greater than the distance from the collision region to the detector.

Crossed-beam collisions exploit the well-defined directionality to enable the experimentalist to measure the angular distribution of atoms or molecules in one beam that have been scattered from those in the other beam and often reveals very important information such as the interaction potential¹³ and dynamics of the reaction.

Figure 2.0: Schematic illustration of supersonic expansion of a gas through a nozzle adapted from “molecular dynamics in free clusters and nanoparticles studied in molecular beams” by Michal Farnik, 2011.

2.2 Universal Detection

During the late 1960s electron bombardment ionization¹⁴⁻¹⁵ became the main technique used as ‘universal detection’ in probing products in molecular beam spectroscopy but its downfall has been the huge interfering background signal that undermined certain important dynamic features of interest as well as having to endure

very long acquisition time.¹⁶⁻¹⁷ In an attempt to overcome this limitation, Lee and coworkers¹⁸ used differential pumping in both the source and detection region of their chamber and it drastically reduced the background interference and enhanced the detection sensitivity in the ionization region although issues about fragmentation of parent species in producing daughter ions still remain a big problem. Single photon ionization usually occurs in the vacuum ultraviolet (VUV) region and has the capability of performing soft ionization of basically all organic compounds. The development of VUV for single photon ionization has been limited by the availability of VUV light sources. In the early 1990, a high-resolution monochromatized third-generation VUV synchrotron source at the chemical dynamics beamline was established. In addition to its universality, the ability to tune the radiation offers it an added advantage of selectivity in the internal energy of the detected species. The first attempt to couple VUV photoionization detection to crossed-molecular beam was carried out by Suits *et al.*¹⁹ in Berkeley by using the synchrotron radiation source at the Advanced Light Source to study reactive scattering of chlorine with propane. There are very limited numbers of synchrotron light sources in the world. However, the need for researchers to locate at one of the world's few source facilities with a VUV synchrotron source is a big challenge. Recently, inspired by synchrotron studies, Casavecchia and coworkers were able to use low energy electrons to probe products in their crossed-beam scattering experiments by tuning the electron energies below that of the dissociative ionization. This reduces fragmentation of the parent species.²⁰⁻²² Over the past few decades there has been major achievement with the production of commercial available inexpensive lasers such as the 157 nm F₂ (7.9 eV) excimer laser. This gives 10-ns-long pulses with the capability of

producing more than 1 mJ per pulse at a repetition rate up to 100 Hz. Davis and his group has utilized the 157 nm excimer laser to study reactions between transition metal atoms with hydrocarbon molecules with very high signal to noise ratio compared to electron impact ionization.²³⁻²⁵ The Suits group has used of 157 nm (7.9 eV) to carry out single photon ionization of alkyl radicals generated from crossed-beam imaging studies of reactions between chlorine and fluorine radicals with very high efficiency due to the fact that, the ionization potential of most of these radicals is below 7.9 eV.²⁶⁻²⁹

2.3 Resonance Enhanced Multiphoton Ionization.

Resonance-enhanced multiphoton ionization (REMPI) is a unique soft photoionization technique that has been used extensively as a selective ionization probe for mass spectrometry. REMPI is a powerful spectroscopic technique, which involves ionization of atoms or molecules by successive absorption of two or more laser photons. This ionization technique relies on the tunability of lasers to ionize molecules with rotational and vibrational state selectivity. In order to achieve ionization using REMPI, the sum of the absorbed photon energy should exceed the ionization energy of the targeted species. The wavelength of the excitation laser can be varied such that a photon can ionize the molecule when it is on resonant with single or multiple photon absorption tuned, exciting the molecule to an intermediate electronic state. Because of a resonance state condition, the multiphoton absorption intensity is enhanced to several orders of magnitude compared to the non-resonant ionization. Various excitation schemes can be used for REMPI, and they are described by the number of photons used for excitation and ionization. For example, in the simplest resonance-ionization scheme one photon is used

to excite the molecule and an additional photon to ionize it, this is known as the (1 + 1) REMPI scheme, also sometimes termed resonant 2-photon ionization or R2PI. The first photon excites the molecule to a higher energetic intermediate state. If the lifetime of the intermediate state is sufficiently long, a second photon is absorbed and elevates the molecule above the ionization threshold. Sometimes, the intermediate state is at an unfavorably high energy for the available laser wavelength and thus can only be reached by absorbing two or even three photons; ionization, subsequently, must be completed by absorbing an additional photon (2+1 and 3+1 REMPI, respectively). Figure 2.1 illustrates ionization REMPI schemes for 1+1 and 2+1 REMPI. Higher order REMPI schemes usually require high photon fluxes to ensure maximum absorption of all photons during the short life of the intermediate state and this causes more fragmentation compared to the 1+1 REMPI scheme. Zare and coworkers performed the first studies on reaction dynamics of Ba + HCl using multiphoton ionization of BaCl.³⁰ Further advancement of REMPI enabled Houston and Chandler³¹ to famously image methyl from the photodissociation of methyl iodide. In their experiment, CH₃I in pulsed molecular beam was dissociated by 266nm Nd:YAG laser, and the CH₃ photofragment was ionized by 2+1 REMPI at 330 nm.

FIGURE 2:1 Schemes for ionization by resonance-enhanced multiphoton ionization (REMPI) (A) One-color, two-photon (1+1) REMPI, (B) 2+1 REMPI

2.4 ION IMAGING

The ion imaging technique allows the spatial distribution of a reaction product species to be visualized directly, yielding the entire three-dimensional angular and velocity distribution of a photolysis or reaction event in a single digital snap shot. Qualitatively, it also provides a direct visualization method of the chemical process. Chandler and Houston³² pioneered the foundation of the state of the art ion imaging technique being used today when they were investigating the photodissociation dynamics of methyl iodide. A typical ion imaging technique involves sending a molecular beam through a small hole of a repeller plate, where it is photodissociated by a photolysis laser. The resulting product molecule is then ionized with a probe laser. The second plate, the extractor, is used together with the repeller to maintain an electric field and direct the three-dimensional ion cloud formed along a time-of-flight tube on to a two-dimensional micro-channel plate (MCP) which is coupled with a fast phosphor screen. Ions striking the front face of the MCP gives rise to a burst of electrons at the back face, as these electrons strike the phosphor screen they produce a flash of light. The pattern of ions striking the MCP is transformed by this process into an image on the phosphor screen, which may can be captured by a CCD camera, digitized and sent to a computer for processing and analysis. A tedious mathematical inversion method (Abel transformation) is often used to reconstruct the 3D distribution in order to extract meaningful information of the 2D projected image. All information (kinetic energy, and angular distributions) is extracted from the spatial appearance of the two-dimensional image, which gives us direct information on the dynamics of the photodissociation event. A major drawback of

this technique was the poor resolution and distorted image acquired due to the use of grids in the aperture of the electrodes. Figure 2.2 shows a pictorial representation of a conventional ion imaging apparatus. In an attempt to overcome this problem Eppink and Parker³³, introduced the velocity map imaging (VMI) in which they removed the grids and instead used the plates as focusing electrodes. This allowed particles with the same initial velocity vector to be mapped onto the same point of the detector irrespective of their point of origin. The lens can also be used to magnify the resulting ion image, although there is the need to calibrate the lens to determine the magnification factor. The magnification increases the energy resolution as the spatial separation of the rings appearing on the detector is increased.

Despite the improvement achieved on the energy resolution, the projection-reconstruction requirement still existed. The use of the inversion process introduces noise in the symmetry axis of the recovered image thereby compromising experimental resolution. The VMI method also requires the system to have cylindrical symmetry in order to retrieve the 3D distribution of the 2D velocity projections. This requirement of the VMI method limits its use particularly when undertaking polarizations experiments. The introduction of slicing was aimed in addressing these challenges. In principle, the central slice of the ion cloud contains the full angular and velocity distribution thereby eliminating need for the Abel transformation method for reconstruction of the image. Kitsopoulos *et al.*³⁴ used delayed pulsed extraction to expand the ion cloud followed by field free expansion to detect the central slice of the ion cloud. The drawback to this technique was the poor resolution of the image due to the introduction of fine mesh on the ion optics assembly and space charge between the ions. The Suits group⁷ introduced

Direct Current (DC) Slice Imaging that addressed the major drawback of the slicing technique of Kitsopoulos *et al.* and permitted VMI conditions to be maintained. The use of grids or pulsed electric field was eliminated and replaced with an additional lens at low voltages to stretch the ion packet in the acceleration region, increasing the arrival time spread onto the detector. This enables the central slice of the ion cloud that contains the translational energy release and the angular distribution to be imaged directly onto the MCP detector. At the same time this led to an additional 10-fold enhancement in velocity focusing compared to standard VMI.

Figure 2.2 Set-up diagram of a conventional photofragment ion imaging apparatus. Diagram adapted from McDonnell *et al.*, *J Mass Spectrum.* 333: 415. John Wiley and Sons. Copyright 1998.

2.5 INSTRUMENT SET-UP

The experiments presented here were carried out in our crossed-beam imaging apparatus as shown in Fig.2.3. The make up of the machine consists of two perpendicular source chambers that are fixed at 90° , and a reaction chamber. The reaction chamber is differentially pumped to a base pressure of 10^{-8} torr to ensure single-collision conditions while the source chambers' pressures are maintained at 10^{-7} torr (base) and operated to a pressure of 10^{-5} torr (beams on) pumped by turbomolecular pumps mounted under each chamber. The radical beam and our target molecular beam are isolated in separate source chambers, and are seeded in various carrier gases (H_2 , He, Ar,) to vary the collision energy. Piezoelectric actuators (stack) and piezoelectric disc valves were pulsed at 10Hz to generate the molecular beam and after supersonic expansion, beams are skimmed into the main reaction chamber. The scattered radical products are immediately ionized after collision in the interaction region with either a VUV excimer laser (F_2 , 7.9eV) or by employing a resonance enhanced multiphoton ionization (REMPI) detection scheme. The product ions are accelerated via a four electrode dc slice ion optics assembly to impact on a 75 mm diameter dual micro-channel plate (MCP) detector coupled to a fast phosphor screen held at 5 KV. The front of the MCP assembly is held at ground potential and the back plate is pulsed to “gate” the central slice of the reaction scattered products at a specific mass by an application of a high voltage pulse (2.2 – 1.2 kV bias, 1200 ns width) using a commercial pulser (DEI PVX-4140). The timing of the pulsed molecular beam, firing of the photolysis and probe lasers, and the detector gate pulse were controlled using a delay generator (BNC 555). The resultant images are recorded using a charged coupled device camera. The dc slice imaging detection scheme and megapixel acquisition

program (NUACQ-2) were used to accumulate the raw images containing centroided data. Background subtraction and density-to-flux corrections were performed prior to transforming the scattered distributions in the center of mass frame.³⁵

Figure 2.3: Schematic view of the crossed-beam apparatus combined with universal sliced dc ion imaging.

2.6 Piezo Stack Valve

Proch and Trickl famously employed piezoelectric disk actuators with a high voltage switch to develop a valve for a molecular beam source.³⁶ Although these valves have short opening times, they still exhibited some shortfalls such as long pulse durations, and low gas throughput. One very important limitation of disk actuators is its low acceleration force, which has a maximum value of only 10 N. This limits the ability of the valve to open large nozzles at higher pressures. Over the last few years our lab has developed a new, robust valve³⁷ based on piezoelectric stack actuators which was inspired by an earlier design of Gentry et.³⁸ Our new design valve shows a better improvement in the pulse duration and molecular densities compared to the disk translators. With our new design we are able to achieve up to 180 μm linear motion of the plunger with pushing and pulling force up to 4500/500 N respectively.

Figure 2.4 shows a schematic view of the valve assembly. It operates through the application of a high voltage pulse to the actuators. In its closed position, a high voltage of +800 V is applied from a high voltage power supply, which delivers an average power of 200 W (Kepco BHK 1000-0.2MG). To open the valve, the actuator is grounded by switching the actuator voltage to 0 V with a fast high voltage transistor switch (Behlke HTS 61-03 GSM) or a DEI pulse generator (pvx-4140) which is combined with a high-capacitance RC circuits ($R = 1\Omega$, $C = 20\ \mu\text{F}$).

We have recently been able to generate a high-density oxygen radical source from SO_2 by attaching a 10 mm long cylindrical quartz tube with an inner diameter of 1 mm to the end of the nozzle of the valve which confines the molecules along the length of the

quartz tube. This enables us to loosely focus a 193 nm excimer laser beam along the quartz tube to initiate photolysis of SO_2 . This generates an intense oxygen beam with the oxygen atom population density increasing by a factor of 3 compared to when we do not have a quartz tube attached to the exit of the nozzle. Figure 2.4 is a schematic view of the valve assembly without the attached quartz tube.

Figure 2.4: Schematic view of the valve assembly. The piezostack actuator is mounted and aligned outside of a stainless steel valve body in a half-cylinder. The valve is sealed by a kalarez o-ring (yellow spots) both at the tip and at half-length of the plunger. Other o-rings are shown in red. The teflon guide is used to form a snug fit that restricts lateral movement of the piezo actuators and prevents any torque. The fine micrometer head is used to regulate the volume of gas through the orifice.

CHAPTER 3

Imaging the inelastic scattering of vibrationally excited NO ($\nu = 1$) with Ar.

Alexander Kamasah¹, Hongwei Li¹, Jolijn Onvlee^{2,3}, Ad van der Avoird³,

David H. Parker⁴, and Arthur G. Suits^{1,*}

¹Department of Chemistry, University of Missouri Columbia MO 65211

² Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY,
Notkestrasse 85, 22607 Hamburg, Germany

³Theoretical Chemistry and ⁴Department of Laser Physics, Institute for Molecules and
Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The
Netherlands

Abstract

The inelastic scattering of vibrationally excited NO ($v=1$) with Ar at a collision energy of $3.0 \text{ kcal mol}^{-1}$ was investigated in crossed beams. Vibrationally excited NO was generated by flash heating and rotationally cooled by the supersonic expansion. The differential cross sections were compared to those of the vibrational ground state NO ($v=0$) with Ar, which were also compared to theoretical calculations for scattering from the ground vibrational level. The differential cross sections show a similar strong j dependence of the rotational rainbow maxima from the inelastic scattering for both NO ($v=0$) and ($v=1$) but no significant differences between NO ($v=0$) and ($v=1$) were seen.

3.1 INTRODUCTION

Inelastic scattering of the open-shell radical NO with rare gases has been a benchmark for understanding collision dynamics for decades, and new aspects continue to be revealed. Nitric oxide is chemically stable and spectroscopically convenient, and has been the target system of choice for experimental studies of NO $^2\Pi$ collision dynamics and energy transfer mechanisms. The $^2\Pi$ ground state of NO follows Hund's case (a) when the rotational quantum number j is small. The spin and orbital angular momentum interact with each other and they form two spin-orbit components with $\Omega = 1/2$ and $3/2$. The lower of the two-orbit levels is noted F_1 and the upper F_2 ; in the low j , case (a) limit, F_1 is $\Omega = 1/2$ and F_2 is $\Omega = 3/2$. The splitting between the two levels is about 125 cm^{-1} . In addition to the spin orbit-coupling, each rotational level is further split into doublet because of the coupling between the nuclear rotation and the electronic orbital angular momentum. This doubling is termed Λ -doubling and spectroscopically, the notation used for these levels is e and f known as the total parity as shown in figure 3.1.

Figure 3.1 Energy level diagram of NO showing the energy splitting between the Λ -doublet components of each rotational level.

Measurements of angular distributions from the scattering experiments directly embody the differential cross sections (DCSs), providing a sensitive probe of the molecular interaction potential energy surfaces (PESs). The application of velocity map imaging combined with crossed-molecular beams has been found to be very powerful in studies of reactive and inelastic scattering to understand the underlying dynamics²⁻³³⁻³⁹ Houston and coworkers first employed imaging to probe the state-to-state DCSs for inelastic collisions of ground state NO ($X^2\Pi$) with Ar.⁴⁰⁻⁴¹ They observed rotational rainbow peaks in the angular distributions and these peaks move to backward scattering angles with increasing final rotational level. This was followed by work from the Suzuki,⁴² and Chandler groups,⁴³ in which fully state-resolved DCSs for the inelastic scattering of NO ($X^2\Pi$, $v = 0$, $j = 0.5$) with Ar were measured resulting from spin-orbit conserving and changing transitions. These arise from scattering from sum and difference potentials built from PESs, of A' and A'' character. Their findings were consistent with quantum mechanical close-coupling (QM CC) calculations based on *ab initio* coupled-cluster CCSD(T) and CEPA potential energy surfaces. Later, Stolte, Brouard and coworkers⁴⁴⁻⁴⁷ were able to resolve the Λ -doublet effects on the DCSs for NO ($X^2\Pi$) inelastic collisions with Ar by coupling a hexapole to the crossed beam velocity map imaging apparatus. They observed different quantum interference structures on DCSs for total parity-conserving and changing collisions. Rigorous quantum scattering calculations suggest that the heteronuclear nature of NO plays an important role in the DCSs for the parity-conserving collisions, but less important for the parity-changing collisions.⁴⁸⁻⁴⁹ Other work by Cline and coworkers⁵⁰ also revealed a high degree of directional preference for NO rotation during collisions with Ar. They reported that the NO product orientation

varies with the deflection angle and for lower rotational states, the variation with deflection angle becomes oscillatory. More recently, van de Meerakker and coworkers in Nijmegen used a Stark decelerator to produce a well-defined and velocity-controlled NO radical beam that intersected with a conventional beam of rare gases. Using velocity map imaging³³, they observed diffraction oscillations in the DCSs from the inelastic scattering of NO radicals with the rare gases He, Ne, Ar, Kr, and Xe.⁵¹⁻⁵² This phenomenon is in excellent agreement with high-level QM CC calculations based on the most accurate PESs.

Although NO inelastic scattering has long been of interest, most such studies have focused on the vibrational ground state and very little has been reported for vibrationally excited NO. The difficulty is very likely due to the challenge of preparing a vibrationally hot but rotationally cold NO molecular beam. Optical pumping has been used to generate the vibrationally excited NO by direct absorption of infrared radiation.⁵³⁻⁵⁵ The rate constants were then measured for NO ($X^2\Pi$, $v = 1, 2, 3$) with selected gas molecules including Ar. The thermally averaged cross-sections were reported for total removal of NO from the particular rovibronic level $X^2\Pi_{1/2}$, $v = 3$, $j = 0.5, 3.5$, and 6.5 in collisions with Ar at various temperatures, 27, 44, 53 and 139 K.⁵³ Alternatively, the Houston group⁵⁶ prepared vibrationally excited NO at the exit of the valve nozzle through a photoinitiated reaction between O(¹D) and N₂O. Due to the nature of the reaction, they were only able to make vibrationally excited NO at $v = 5$. They measured the DCSs for rotationally inelastic scattering ($j = 6.5, 16.5$ and 20.5) of vibrationally excited NO ($v = 5$) from Ar for the first time by coupling crossed molecular beams with velocity map imaging. On comparing the results of $v = 5$ to $v = 0$, they observed a small shift in

rotational rainbow maxima to smaller angles in $v = 5$ compared to the ground state $v = 0$. They concluded that the shift in the rainbow angle is a manifestation of the increased angular anisotropy during vibrational excitation.

In the present work, we prepared the vibrationally excited NO ($X^2\Pi$, $v = 1$) by resistively heating the nozzle of our valve. We present the results of our crossed-beam study on vibrationally excited NO ($X^2\Pi$, $v = 1$) with Ar by acquiring images for the inelastic scattered NO products using our DC slice imaging technique. After background subtraction and density-to-flux correction, the differential cross sections for various j -levels of NO ($v = 1$) are derived to unravel the underlying dynamics, and compared to that from the inelastic scattering of NO ($v = 0$) with Ar under same conditions.

3.2 EXPERIMENTAL SECTION

The experiments are carried out in a crossed molecular beam apparatus combined with DC slice ion imaging, which has been previously described elsewhere⁵⁷. The apparatus consists of one reaction chamber and two source chambers that are perpendicular to each other. The Ar beam is pulsed at 10 Hz with a backing pressure of 5.3 bar into one source chamber via a piezoelectric stack actuator (Physik Instrumente, P212.80) valve³⁷ with 120 μm poppet translation and 50 μs pulse duration. The vibrationally excited NO is generated with a home-built flash pyrolysis⁵⁸ source closely related to the pyrolysis design by Chen and coworkers⁵⁹. The NO beam is introduced into the second source chamber by pulsing a piezoelectric pulsed valve operating at 10 Hz with a backing pressure of 5 bar. The NO beam is expanded into the SiC nozzle and resistively heated to $\sim 1200\text{K}$ with a DC power supply (supplying a current of 1.6 A at a

potential of 17 V). The vibrationally excited NO ($X^2\Pi$, $v = 1$) is prepared and then rotationally cooled to ~ 20 K before entering into the interaction chamber to be intersected by the Ar beam at 90° . The final scattered NO ($X^2\Pi$, $v''=0$ or 1) products are then state-selectively ionized using $(1 + 1)$ resonance-enhanced multiphoton ionization (REMPI) near 226 nm via the $A^2\Sigma^+(v'=0 \text{ or } 1)$ electronic state and detected with the DC slice ion imaging technique. The UV radiation near 226 nm is generated by the frequency tripling of the fundamental output of a pulsed dye laser (Sirah Cobra-Stretch, LDS 698 dye) pumped by the second harmonic of a seeded Nd:Yttrium aluminum garnet (Nd:YAG) laser (Quanta Ray, Spectra Physics). A four-electrode dc slice ion optics assembly accelerates the ions in the direction perpendicular to the scattering plane. After passing through a 75 cm field-free flight tube, the NO^+ ions are velocity focused onto a dual microchannel plate (MCP)/phosphor screen coupled detector. The detector is gated for the center slice of the scattered product ions and resultant images are recorded using a charge-coupled device (CCD) camera and analyzed with our data acquisition program. The background signal from the NO beam alone is subtracted and density-to-flux correction is performed before further analysis to obtain the angular distributions of the rotationally inelastic scattering.

THEORY SECTION

We performed QM CC calculations to compute state-to-state cross sections for NO ($v=0$) + Ar. A scattering program for open-shell diatom-atom scattering was used that was originally developed for OH + rare gas collisions⁶⁰. The ab initio potential energy surfaces constructed by Alexander were used as input⁶¹. Using the renormalized

Numerov method, we propagated the wave function on an equidistant grid in R from 3.5 to 50 Bohr with 1094 points, where R is the distance between the Ar atom and the center-of-mass of the NO molecule. We took all NO rotational levels up to $j = 25.5$ and all partial wave contributions up to a total angular momentum of $J = 200.5$ into account in the channel basis set. The scattering cross sections were computed for a collision energy of $3.0 \text{ kcal mol}^{-1}$ and for initial NO rotational levels up to $j = 6.5$.

3.3 RESULTS AND DISCUSSION

In this present work, the NO products at various rotational j levels are detected after inelastic collisions of NO ($v = 0, 1$) with Ar at a collision energy of $3.0 \text{ kcal mol}^{-1}$. The experimental scattering results for the ground state NO ($v = 0$) with Ar were compared to the theoretical results. Further comparison was conducted on inelastic scattering of the vibrationally excited NO ($v = 1$) to the ground state NO ($v = 0$) under the same conditions. This study is directed to examining whether the different vibrational excitation of the diatomic molecule affects the angular distributions of the rotationally inelastic scattering under the same conditions. Superelastic scattering of NO ($v = 1$) giving ($v = 0$) product was not expected or observed, as it is a process of much smaller total cross section.

We first measured REMPI spectra for NO to characterize the NO molecular beam generated from the flash pyrolysis source. The 1+1 REMPI spectra of $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ and $(1,1)^{62-63}$ bands were obtained at two different energy regions, corresponding to two different prepared vibrational levels for NO, $v = 0$ and $v = 1$, respectively (as shown in Fig.3.2). The rotational band contour is simulated with known parameters⁶⁴⁻⁶⁶ under the

rotational temperature of 20 K using the PGOPHER program⁶⁷. The good agreement of the REMPI spectra for both NO $\nu = 0$ and $\nu = 1$ between experimental and simulated results (as shown in Fig. 1) indicates that the generated NO beam is rotationally cold, ca. 20 K. At this rotational temperature, only the first few rotational levels ($j = 0.5$ to 5.5) are significantly populated for our NO molecular beam source at both $\nu = 0$ and $\nu = 1$, and these rotational levels thus dominate the inelastic collisions we observe with Ar. The final rotational states populated by inelastic scattering are ionized by 1 + 1 REMPI employing main R_{11} branch (overlapping with the Q_{21} satellite branch) of the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition. The vibrational ground state NO $\nu = 0$ is probed using the (0,0) band, while the vibrationally excited state NO $\nu = 1$ is probed using the (1,1) band. The inelastic scattering images of the final rotational states for NO $\nu = 0$ and $\nu = 1$ are shown in Fig. 3.3 with the nominal Newton diagrams superimposed on them. The images portray the forward scattered signal pointing down (the direction of the NO beam) and the backward scattered signal pointing up. The background signal arises from NO in the molecular beam that does not undergo inelastic collisions with Ar. This background

Figure 3.2 $1 + 1$ REMPI spectra of NO recorded for $v = 0$ (top panel) using (0, 0) band and $v = 1$ (bottom panel) using (1, 1) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. The lower spectra (blue) are the simulation at 20 K, while the upper spectra (black) are experimental results.

is more intense for lower j levels because of the low rotational temperature (~ 20 K) for our molecular beam. Therefore, the present study focuses on only high j levels, from 12.5 to 22.5, in order to reduce the interference in the inelastic scattering from the background.

Figure 3.3. DC slice images for inelastic scattering of NO with Ar after background subtraction and density-to-flux correction at a collision energy of 3.0 kcal/mol with Newton diagram superimposed. First two upper panel compares the scattering images for $v = 1$ to $v = 0$, for $j = 12.5$, 14.5, and 16.5, while the Lower two panels compares also compares $v = 1$ to $v = 0$, for $j = 18.5$, 20.5, and 22.5.

The images in Fig. 3.3 show a single sharp scattering ring for each j level except for $j = 20.5$ after the inelastic collision between NO and Ar. The size of the image decreases with increasing j , which is consistent with the conservation of energy. The inner ring of the image labeled $j = 20.5$ corresponds to signal at the $j = 20.5$ level whereas the outer ring corresponds to $j = 15.5$, since the $R_{11}(20.5)$ transition is very close to the $R_{21}(15.5)$ transition. Therefore, this image is analyzed to yield two separate DCS's. The center-of-mass angular distribution is obtained by integrating the signal over a certain radial region of interest to characterize the rotationally inelastic scattering. We first compared the experimental angular distribution of NO($v = 0$)/Ar system with the theoretically predicted differential cross sections (DCS) for this system at different j levels. At present only the $v = 0$ DCS is available for this system. In order to match our experimental condition of 20 K rotational temperature, each effective DCS distribution is generated by weighting the initial j states of NO $v = 0$ with a Boltzmann distribution at 20 K.

Both experimental and theoretical DCS distributions (as shown in Fig. 3.4) of NO($v = 0$)/Ar system exhibit the expected rotational rainbow peak that shifts to larger scattering angle with increasing rotational excitation. We observed forward scattering for $j = 12.5$ to 14.5 with the rotational rainbow maxima around 35° and 50° respectively. Sideways scattering was observed for $j = 15.5, 16.5, 18.5$, and 20.5 with the rotational rainbow maxima shifting to larger angles, and backward scattering was seen for our highest detectable $j = 22.5$ level with collision energy of $3.0 \text{ kcal mol}^{-1}$. We see evidence of the double rainbow phenomenon as predicted by theory, with two rainbow peaks around 60° and 120° for $J = 15.5$ and 16.5 , despite averaging over the initial 20K rotational distribution. This arises from scattering off either the O end or the N end of the

Figure 2.4 A comparison of the experimental and theoretical differential cross sections for the scattering of NO ($v = 0$) with Ar for the indicated final rotational level. The black circles represent the experimental results and the blue triangles represent the theoretical predictions.

molecule. These two peaks are more clearly resolved for $J=15.5$, but the more forward peak is significantly reduced compared to theory. This may be due to interference from $J=20.5$ which is also present in the image and enhances the more backscattered peak. We then investigate whether vibrational excitation of the NO molecule significantly affects the angular distributions of the rotationally inelastic scattering with Ar. The experimental differential cross section for a particular final rotational state in the $\text{NO}(\nu = 1)/\text{Ar}$ system is compared to that in the $\text{NO}(\nu = 0)/\text{Ar}$ system in Fig. 3.5. The signal-to-noise level of the $\text{NO}(\nu = 1)/\text{Ar}$ system is lower than that in the $\text{NO}(\nu = 0)/\text{Ar}$ system as may be seen. Nevertheless, the differential cross sections still show a rotational rainbow peak shifting to larger scattering angle for $\text{NO } \nu = 1$. We also see that the position of the rainbow maxima for $\text{NO } \nu = 1$ at each final rotational state almost tracks that of $\text{NO } \nu = 0$. There is only one significant exception, that is $j = 12.5$. At $j = 12.5$, a modest enhancement of the backward scattering distribution is obtained in the $\text{NO}(\nu = 1)/\text{Ar}$ system which we do not observe for the $\text{NO}(\nu = 0)/\text{Ar}$ system nor in the theoretical DCS for $\text{NO}(\nu = 0)$. Aside from this level, the comparison of $\nu = 1$ to $\nu = 0$ does not reveal significant differences in the scattering distributions within the present signal-to-noise. The results obtained might not be that surprising since we only excite NO to $\nu = 1$, and the equilibrium bond length is only $\sim 1\%$ larger. Houston and coworkers observed only a small change in the angle of the rainbow maxima in the scattering of vibrationally excited $\text{NO}(\nu = 5)$ with Ar compared to the scattering of NO in the vibrational ground state with Ar. However, the root-mean-square spread in the N-O distance is $\sqrt{3}$ times larger for $\nu = 1$, suggesting an effect might be observable. It may be that by averaging over the 20 K distribution we

obscure small changes in the DCS. Future studies that employ spectroscopic preparation of vibrationally excited levels while maintaining a rotationally very cold beam may have an improved chance of revealing subtle effects.

Figure 3.5 Comparisons of the experimental differential cross section distributions for the inelastic scattering of NO($v = 0$)/Ar (black curve) and NO($v = 1$)/Ar (red curve). Top panel compares $v = 1$ to $v = 0$ for $j = 12.5, 14.5, 15.5, 16.5$, and down panel compares $v = 1$ to $v = 0$ for $j = 18.5, 20.5$, and 22.5 .

3.4 CONCLUSION

We have used crossed molecular beams coupled to dc slice velocity map imaging to investigate the effect of vibrational excitation on the inelastic scattering for NO with Ar. The inelastic collision process with collision energy of $3.0 \text{ kcal mol}^{-1}$ for vibrationally excited NO at $v = 1$ with Ar is examined and compared to that of the vibrational ground state NO with Ar. We observed the expected gradual shift of the rotational rainbow maxima to larger scattering angle as we probe higher rotational levels. Within the signal-to-noise, we did not observe significant scattering differences between the NO($v = 1$)/Ar and NO($v = 0$).

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CHAPTER 4

Intersystem crossing in the exit channel

Hongwei Li, Alexander Kamasah, Arthur G. Suits*
Department of Chemistry, University of Missouri, Columbia, MO
65211, USA

Abstract

Intersystem crossing (ISC), the non-radiative transition between two states with different multiplicity, plays an important role in photophysics, photochemistry, and photobiology. ISC is generally understood to be efficient when heavy atoms are present due to the strong spin-orbit coupling, or when strongly bound long-lived complexes are formed that increase the chance of finding the singlet/triplet intersection seam. Here we present evidence for a different ISC mechanism in the bimolecular reaction of O (^3P) with the alkylamines. In crossed-beam experiments, the product velocity-flux maps are measured for aminoalkyl radicals produced from H-abstraction on the methyl group giving OH radicals as co-fragments. Low product translational energy release and isotropic angular distributions indicate that such reactions undergo complex formation first before producing OH and aminoalkyl products. However, there is no well on the triplet potential energy surface that could support such a complex. *Ab initio* calculations suggest instead that ISC occurs in the exit channel region due to the long-range dipole-dipole interaction between the nascent radical product pair coupled with the vanishing singlet-triplet splitting at long range. ISC then leads to a deep hydroxylamine well before OH elimination.

4.1 INTRODUCTION

Intersystem crossing (ISC), the non-radiative transition between two electronic states with different spin multiplicity, is ubiquitous and important in fields ranging from chemical physics to chemical biology. ISC is involved in a wide range of applications including materials science⁶⁸, molecular photonics⁶⁹, photosensitizers⁷⁰, and photodynamic therapy for cancer⁷¹. It is well studied that the “heavy-atom effect” promotes ISC since the inclusion of heavy atoms in the molecular structure enhances the spin-orbit coupling between singlet and triplet states.⁷²⁻⁷³ ISC is also observed in oxygen atom reactions with unsaturated hydrocarbons, in which case the strongly bound addition complex is long-lived, increasing the probability for the system to the singlet/triplet seam of intersection where ISC occurs.⁷⁴⁻⁷⁹ Here, we show that, even in the absence of heavy atoms or a strongly bound adduct on the initial triplet potential surface, ISC occurs in the course of bimolecular reactions of O(³P) with amines. In this case, we propose that ISC is promoted by the near-degeneracy of the singlet and triplet potential surfaces in the exit channel, along with the long-range dipole-dipole interaction and high dimensionality of the system that permits a brief period of recollision, leading finally to the deep hydroxylamine well on the singlet surface.

Amines, prototypical nitrogen-containing compounds, are found in the conventional fuels, such as coal, and renewable energy sources, such as biomass and biofuels.⁸⁰⁻⁸¹ Burning of these nitrogen-containing compounds in the fuel is a principal source of nitrogen oxides (NO_x) emitted to the atmosphere.⁸⁰⁻⁸² NO_x represents NO, NO₂, and N₂O that are harmful to the atmosphere, involved in formation of photochemical smog and acid rain, and N₂O is also an effective greenhouse gas.⁸⁰⁻⁸² The combustion chemistry of

nitrogen compounds has been explored for decades, focusing on kinetic rate measurements, nitrogen conversion mechanism, and intermediates formed during the reaction and their roles in the overall process.⁸⁰⁻⁸³⁻⁸⁴⁻⁸¹⁻⁸² However, a clear understanding of the reaction dynamics for nitrogen compounds, especially in the early step of the combustion process, is limited but desired to assist the successful development of accurate models for real combustion chemical systems.

Here, we investigated the mechanism of the elementary reactions in the initial combustion process, reaction of O (^3P) radical with amines, dimethylamine (DMA) and trimethylamine (TMA). We have characterized the translational energy release and angular distributions during the reactions using crossed beam scattering combined with universal DC slice imaging as described previously⁸⁵ and in Supporting Information (SI). *Ab initio* calculations on the energies and structures along the reaction pathways were also performed to gain insight to the underlying dynamics. Combining these experimental and theoretical studies suggests that ISC from triplet to singlet potential energy surfaces plays an important role in the bimolecular reaction dynamics for O (^3P) reaction with amines.

4.2 EXPERIMENTAL

The electronic ground state atomic oxygen, O (^3P), was generated from the photolysis of SO_2 by 193 nm radiation. Amines (DMA or TMA) seeded in helium were crossed with the O (^3P) beam at 90° under single-collision conditions. The scattered products from the bimolecular reaction were ionized at the interaction region by an F_2 excimer laser (157 nm, 7.9 eV). The ions were then accelerated onto a position-sensitive detector that is gated to select a specific m/z ratio. The resultant ion images were recorded

using a charge-coupled device camera, employed with a high resolution real-time ion counting method using our megapixel acquisition program NuACQ.⁸⁶ The sliced and centroided images were accumulated, reflecting the product velocity-flux contour maps with the speed and angular information for the reaction.

Figure 4.1 DC slice images top Dimethylamine (DMA) and bottom Trimethylamine (TMA) with Newton diagrams superimposed, with O (^3P) after background subtraction and density-flux-correction at collision energies of 7.8 and 8.0 kcal mol $^{-1}$, respectively.

4.3 RESULTS AND DISCUSSION

For the bimolecular reaction of O (^3P) with TMA at a collision energy of $E_{\text{coll}} = 8.0 \text{ kcal mol}^{-1}$, we detected only one product channel m/z 58 under our experimental conditions. This mass channel represents $(\text{CH}_3)_2\text{NCH}_2$ radical formed with hydroxyl radical (OH) co-fragment after TMA is attacked by the O (^3P) atom. The corresponding product scattering image after background subtraction and density-to-flux correction is shown in Figure 4.1 with a Newton diagram superimposed. The scattered radical products are examined in three distinct center-of-mass (*c.o.m.*) angular ranges defined with respect to the TMA beam direction: forward (FW, $0\text{-}60^\circ$), sideways (SW, $60\text{-}120^\circ$) and backward (BW, $120\text{-}180^\circ$). Although the FW component is obscured by a strong photochemical background, the SW and BW components clearly reveal the underlying dynamics. The *c.o.m.* translational energy release distributions $P(E_T)$ of both SW and BW components peak at low energy, $\sim 10\%$ of the collision energy (bottom panel in Figure 4.2). The *c.o.m.* angular distribution $T(\theta)$ (middle panel in Figure 4.2), including both SW and BW contributions, is flat, consistent with the isotropic image observed. These experimental results clearly indicate an indirect reaction mechanism. Formation of a long-lived adduct in a bimolecular reaction results in product translational energy distributions that peak at low energy because of randomization of the internal energy over the vibrational degrees of freedom in the complex. Additionally, if the complex lifetime is much longer than its rotational period, the system loses reference to the initial approach direction, giving rise

Figure 4.2 Center-of-mass angular $T(\theta)$ (top) and translational energy $P(E_T)$ (bottom) distributions for the reactions of O (3P) with TMA (left) and DMA (right) at collision energies of 8.0 and 7.8 kcal mol $^{-1}$, respectively. The sideways (60-120°) component is in blue, and backward in purple (120-180°). The $P(E_T)$ are fitted by least squares polynomial regressions. The $T(\theta)$ are shown averaged every 10° with error bars ($\pm\sigma$) estimated by mean absolute deviation of the raw data in the corresponding angle range.

to a symmetric scattering in the FW and BW directions and identical translational energy distributions in all directions. For complicated polyatomic systems in which the scattering is non-planar, this symmetric scattering becomes fully isotropic.²⁷ Therefore, the low translational energy release and isotropic angular distributions of the scattered products indicate the importance of the complex-elimination mechanism in bimolecular reaction of O (³P) atom with TMA.

The reaction of O (³P) with DMA was also explored at collision energy of 7.8 kcal mol⁻¹. A single product at *m/z* 44 was detected under our experimental conditions (shown in Figure 4.1). This indicates an H abstraction pathway producing C₂H₆N radical in this reaction. There are two isomers for the C₂H₆N radical, CH₃NHCH₂ arising from H abstraction at the methyl site, and N(CH₃)₂ produced by abstraction at nitrogen. *Ab initio* calculations performed using the CBS-QB3 method⁸⁷ implemented in the Gaussian09 quantum chemistry software package⁸⁸ were used to determine ionization energies (IEs) for these product radicals. The calculations predict that CH₃NHCH₂ radical has a vertical IE of 6.7 eV, easily accessed with our detection limit of 7.9 eV, whereas N(CH₃)₂ radical has a much higher vertical IE (9.5 eV). Therefore, only CH₃NHCH₂ radical product is detected under our experimental conditions, even though the N(CH₃)₂ radical is also a possible product from this reaction. This inference was also proved by checking the reaction of O (³P) with the partially deuterated isotopologue (CD₃)₂NH (see SI). Only the CD₃NHCD₂ radical product was observed by our 7.9 eV probe, consistent with the ionization energy calculations. This indicates the H/D removal by O(³P) radical we detected occurs at the methyl site rather than the amine site. Similar low translational energy release and isotropic angular distributions were also obtained here for the

Figure 4.3. Key points on the triplet (red) and singlet (black) PESs of the $\text{O}(^3\text{P}) + \text{TMA}$ reaction. The diagram has been calculated at the CBS-QB3 level of theory. Relative energies are shown in kcal mol^{-1} . The purple dashed line illustrates the barrierless direct H abstraction pathway on the triplet surface with ISC occurrence indicated by a blue circle.

deuterated (in SI) and non-deuterated (in Figure 4.6) systems, confirming again that the complex-elimination mechanism plays an important role in bimolecular reactions of O (^3P) with amines to produce OH. The complex-elimination mechanism observed here agrees well with the previous cross-jet reactor study and kinetic measurements performed decades ago for the title reactions.⁸⁹⁻⁹⁰

The crucial underlying question now is the pathway for OH elimination from the complex. A careful search along the triplet and singlet potential energy surfaces (PESs) was performed by *ab initio* calculations at the CBS-QB3 level of theory. For the triplet PESs of the O (^3P) + TMA reaction as shown in Figure 4.3, we could not locate any transition state (TS) for the direct H abstraction pathway to generate OH and $(\text{CH}_3)_2\text{NCH}_2$ products that we probed experimentally. This suggests that the direct reaction is barrierless. Interestingly, we find a roaming-type TS that has one low imaginary frequency (200 cm^{-1}) indicating a flat PES in this region, and two very low bound frequencies (40 and 50 cm^{-1}) corresponding to motions of the O atom relative to the TMA fragment. This roaming-type TS connects two shallow van der Waals complex wells, $\text{O}\dots\text{N}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{NCH}_2\dots\text{OH}$ in the reaction pathway. However, based on the fact of the observed long-lived complex formation and relatively high collision energy $E_{\text{coll}} = 8.0\text{ kcal mol}^{-1}$ in the experiment, this shallow well is not likely a key aspect of the reaction. We then searched through the singlet PESs since the coupling between singlet and triplet PESs inducing ISC is ubiquitous in chemistry and it is widely observed in O(^3P) reactions with unsaturated hydrocarbons, such as C_2H_4 and CH_2CCH_2 .⁹¹⁻⁷⁵⁻⁷⁷ As shown in the singlet PESs for the O (^3P) + TMA reaction in Figure 4.3, one TS (TS1) and two very deep complex wells ($\text{ON}(\text{CH}_3)_3$ and $(\text{CH}_3)_2\text{NCH}_2\text{OH}$) are located on the

reaction pathway to form the probed products. However, TS1 found here has a very high barrier energy, 45 kcal mol⁻¹ above the O(³P) + TMA reactant asymptotic limit. Given the experimental collision energy of 8.0 kcal mol⁻¹, the system does not have enough energy to surmount this barrier to form the detected products if the reaction accesses the singlet ON(CH₃)₃ entrance complex well via ISC. Therefore, the only plausible pathway for the reaction will be that the O (³P) radical attacks TMA to initiate direct H abstraction from methyl group. Then, due to the long-range dipole-dipole interaction and the high dimensionality of the system, OH and (CH₃)₂NCH₂ radicals do not part immediately but undergo multiple collisions. At the region where both triplet and singlet PESs have similar energy (as indicated by the blue circle in Figure 4.3), the system hops from triplet to singlet surface and then falls into a very deep hydroxylamine well, forming (CH₃)₂NCH₂OH 100 kcal mol⁻¹ lower in energy than the reactants. The system will stay in the (CH₃)₂NCH₂OH well for a time much longer than its rotational period of the complex, then eliminate OH radical. In this case, the reaction mechanism features ISC *leading to* long-lived complex formation rather than being caused by it.

The PES for the O (³P) + DMA reaction calculated at same level of theory is analogous to the O (³P) + TMA system as shown in Figure 4.4. No TS is found for the direct H abstraction channel, but a roaming-type TS is located between two shallow van der Waals complex wells along the reaction pathway on the triplet surface. However, again the roaming pathway may not play a key role due to the high collision energy and the possibility of barrierless H abstraction. On the singlet surface, two deep complex wells are present on the pathway forming the detected products, but the TS barrier on this pathway again is too high (46.9 kcal mol⁻¹) to surmount given the 7.8 kcal mol⁻¹

Figure 4.4. Key points on the triplet (red) and singlet (black) PESs of the $O(^3P) + DMA$ reaction, calculated at the CBS-QB3 level of theory. Relative energies are shown in kcal mol^{-1} . The purple dashed line illustrates the barrierless direct H abstraction pathway on the triplet surface with ISC occurrence indicated by a blue circle.

experimental collision energy. Therefore, analogous to $O(^3P) + TMA$ reaction, the $O(^3P) + DMA$ reaction may proceed via direct H-abstraction from a methyl group on DMA, followed by ISC to singlet surface leading to the very deep exit channel complex well (CH_3NHCH_2OH) before OH elimination to produce the detected radicals.

To understand the nature of ISC in the present case, we recall that the singlet and triplet surfaces are degenerate at long range for the pair of doublet radical products. In Figure 4.5, a representative structure that would follow the initial H abstraction is shown. Here, we calculate only 10 cm^{-1} energy splitting between the singlet and triplet states. If this initial abstraction leads to a period of recollision, as is commonly seen in polyatomic molecules, particularly given the high dimensionality of the system and the substantial dipole-dipole interaction in this case, the intersection seam of the singlet and triplet surfaces will be crossed many times. This permits ISC and access to the very deep well on the singlet surface. Although direct abstraction is possible on the triplet surface, the absence of a direct component in the experiment suggests that this reaction-mediated ISC is very efficient in this case.

Figure 3.5 Geometric structure calculated at the wB97XD/6-311G(2d,d,p) level of theory.

ISC in O (^3P) reactions with unsaturated hydrocarbons has been well documented, and provides a clear contrast to what is seen here.⁷⁴ Trajectory surface hopping calculations from Bowman and coworkers clearly revealed the mechanism in that case.⁹¹⁻⁷⁵ For O (^3P) + ethylene, there is a diradical addition complex bound by 25 kcal mol⁻¹ that supports a long-lived complex. The bound diradical system hops to the nearby singlet potential surface where that configuration is a transition state connecting oxirane and acetaldehyde. Once on the singlet surface, a number of product channels are open to it. A key feature these two mechanisms have in common is presence of two radical sites that are weakly coupled: for O (^3P) + ethylene it is within the $\cdot\text{OCH}_2\text{CH}_2\cdot$ diradical, while for O (^3P) + TMA it is the two radicals $\cdot\text{OH}$ and $\cdot\text{CH}_2\text{N}(\text{CH}_3)_2$ interacting in the exit channel.

4.4 CONCLUSION

In conclusion, we have investigated the dynamics of the H-abstraction process from the methyl group of amines (TMA and DMA) when reacting with ground state O (^3P). The characterization of the low product translational energy release and isotropic angular distributions indicates that such reactions undergo complex formation first before producing OH and aminoalkyl products. *Ab initio* calculations indicate that the reaction is initiated by direct H abstraction from O attack, and then proceeds via ISC to the singlet surface forming a long-lived complex before OH elimination. This mechanism is not exclusive to amine reactions, and similar dynamics may occur in a large range of related systems yet to be studied.

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CHAPTER 5

Imaging H abstraction dynamics in crossed molecular beams: O (^3P) + propanol isomers

Hongwei Li, Alexander Kamasah, Arthur G. Suits*

Department of Chemistry, University of Missouri Columbia, MO 65211, United States

ABSTRACT

The crossed beam reaction dynamics of ground state $O(^3P)$ atoms with propanol isomers (1-propanol and 2-propanol) have been studied for the first time using the velocity map imaging technique. The hydroxypropyl radical products, generated from H-abstraction of the secondary and tertiary C-H groups of propanol isomers, were detected via single photon ionization at 157 nm under single collision conditions with collision energies of 8 and 10 kcal mol⁻¹. Direct rebound dynamics were reflected by the angular distributions, that show sideways-backward scattering but more favorable backward scattering for both reactions under all collision energies detected here. All the translational energy distributions are peaking at low energy region, on average 20%-30% of the total available energy, indicating high internal excitation in the products. A “vertical” H abstraction mechanism was used here to address the internal excitation of the hydroxypropyl radicals.

5.1 INTRODUCTION

There has been a great amount of interest in reactions involving ground state oxygen atoms with hydrocarbons due to the very important roles they play in combustion⁹²⁻⁹³ and atmospheric chemistry.⁹⁴ A very important mechanism that these reactions undergo is the hydrogen abstraction of which a lot of work has been reported. Luntz and Anderson⁹⁵ coupled LIF to crossed molecular beams to probe OH rotational state from a series of saturated hydrocarbons. They reported that the vibrational state distribution of the nascent OH depends on what type of the hydrogen is abstracted but the final rotational distribution of OH was the same for all types of hydrocarbons. Similar work by⁹⁶, this time involving unsaturated hydrocarbon with O (³P) also confirmed the importance of hydrogen abstraction in the reaction mechanism. In their work, they observed very small rotational excitation of the nascent OH. Suits and coworkers⁹⁷ carried out imaging studies of O(³P) with a series of saturated hydrocarbons by obtaining differential cross sections and translational energy and observed a backward sideways scattering angular distribution of the alkyl products with low average translational energy release. A further study by Suits and coworkers⁹⁸ involving pentane and O (³P) and O (¹D) revealed very contrasting dynamics, while backwards scattering was observed for O(³P), they observed isotropic and forward scattering for the O (¹D) reaction. Lee and his group employed crossed molecular beam with photoionization mass spectrometry to study the reaction dynamics of O (³P) with benzene and its deuterated analogs by measuring the velocity distribution and the angular distribution of the reaction products. They concluded in their report that, oxygen addition and hydrogen elimination were the

major reaction pathways for this reaction. The Casavecchia group⁹⁹ also carried out both experimental and theoretical calculation of O (³P) with propene by combining crossed-molecular beam with mass spectrometric detection and reported the importance of intersystem crossing in such class of systems which accounted for 20% of the product yield. Although the dynamics of RH reactions with O (³P) have been studied extensively, that cannot be said for the oxygenated hydrocarbons especially alcohols (ROH). Over the past few decades, there has been great interest in alcohols for combustion processes¹⁰⁰⁻¹⁰³ as an alternative form of fuel because of its environmentally friendly nature. Although the kinetics and rate of these reactions are very well documented¹⁰⁴⁻¹⁰⁷, there has been limited dynamics study for these reactions. Most of the reaction dynamics of these systems focused on reactions with Cl, F and OH radicals. Osman and his group¹⁰⁸ carried out an ab initio quantum chemical studies of H abstraction from 2-propanol by OH radical and reported that collision-controlled mechanism may play a significant role in the H α abstraction of the reaction. Tully and his group¹⁰⁹ determined the absolute rate coefficient for the reaction between methanol and OH radical by obtaining branching ratio for the reaction, their results showed that at low temperatures H abstraction from the methyl dominates and at high temperature H abstraction is favored on the hydroxyl hydrogen. Taatjes and coworkers¹¹⁰ used time-resolved infrared absorption spectroscopy to study the reaction between Cl atoms with ethanol and its deuterated forms by measuring the absolute rate coefficient, in their work, they reported that the reaction proceeds predominately by H α and the co-fragment HCl produced was vibrationally excited. Recently our group studied the dynamics of F atom with 1-propanol by probing the alkoxy radical. The results showed the backward translational energy peaking at a higher

energy than the sideways and a forward component was observed for the center of mass angular distribution¹¹¹.

Suits and coworkers have carried out detailed dynamic studies of Cl atom reactions with a series of alcohol by using slice imaging. In one of their work, they combined crossed molecular beams with velocity map imaging to probe the alkoxy radicals of methanol, ethanol, and isopropanol reactions with Cl ($2P^{3/2}$). Their results revealed that about 30-40% of the available energy of the reaction was channeled into product translation and the center of mass angular distribution showed a sideways and backwards distribution, an indication of a rebound mechanism¹¹². A recent work by Estill et. al¹¹³ also from the group studied the interaction of chlorine radicals with butanol and its isomers at low and high collision energy. The results revealed backward scattering distribution with respect to the alcohol beam at low collision energy and the scattering distribution shifts to forward direction with increase in collision energy. The results also revealed that about 80% of the collision energy was seen in the forward scattered product for high collision energy. The Zare group¹¹⁴ performed state-to-state dynamics of Cl reactions with methanol at 5.6 kcal/mol collision energy by looking at the rovibrational state distribution of the nascent HCl. They concluded in their work that about 84% of the product HCl was formed in the $v=0$ with the remaining 16% in $v=1$ state. The angular distribution of the products HCl($v=1$) showed forward scattering with very little internal energy of CH_2OH , while significant amount of internal energy was observed for $v=0$ an indication of stripping mechanism for $v=1$. Quantum state differential cross sections of the reaction between chlorine atoms and methanol was studied by Murray and coworkers¹¹⁵ by imaging HCl at different rotational levels in their

vibrational ground state. They observed both forward and backward scattering distribution. At lower J, scattering was in the forward component and shifts to backwards scattering for higher J.

To our best of knowledge, very limited or no dynamic studies work has been carried out on O (^3P) reactions with alcohol. The only dynamic studies that has been reported so far involve O (^1D) reactions with methanol and ethanol and its isotopologue by Goldstein and Wiesenfeld¹¹⁶ where they used LIF to probe the vibrational distributions and product ratios of OH and OD. They reported that the insertion/elimination was the main mechanism by which O (^1D) attacks the alcohol and the attack occurs at the O-H bond, although some may occur at the C-H bond. Based on the low vibrational excitation of the OH(OD), they concluded that the abstraction process was a minor process. Here we present a preliminary reaction dynamics study of H-abstraction reactions of O (^3P) with 1-propanol, 2-propanol using our crossed-molecular beam dc slice imaging. The product hydroxyalkyl radicals were probed via single photon ionization at 157 nm and their images recorded and analyzed after density-flux correction and background subtraction.

5.2 EXPERIMENTAL DETAILS

The scattering experiments were carried out in a crossed molecular beam apparatus combined with a DC slice ion imaging, which has been previously described elsewhere²⁶⁻¹¹⁷. The apparatus consists of a reaction chamber and two source chambers that are perpendicular to each other. Both molecular beams were produced in a separate supersonic expansion in the two source chambers ($\sim 10^{-7}$ torr base pressure and $\sim 10^{-5}$

torr operational pressure) and skimmed into the reaction chamber. Photolysis of SO₂ by a 193 nm excimer laser was used to generate O (³P) atom and it is known that this does not produce any O (¹D).¹¹⁸⁻¹¹⁹ A 5% SO₂ (≥99.9%, Sigma-Aldrich) seeded in He was pulsed from a piezoelectric stack valve³⁷ with a 120 μm translational actuator and 50 μs pulse duration. 1 mm diameter capillary tube was mounted on the exit of the nozzle plate of the stack valve, and 193 nm radiation (from a GAM ArF excimer laser) was loosely focused onto the capillary to photolyze SO₂ to generate a very intense O (³P) beam. Another piezoelectric disc valve was used to pulse 1-propanol or 2-propanol (≥99.9%, Sigma-Aldrich) molecular target beam. By seeding them 5% in He or H₂, the collision energy was changed from 8 kcal mol⁻¹ to 10 kcal mol⁻¹. The scattered hydroxyalkyl radical products were ionized with a F₂ excimer laser (157 nm, 7.9eV) as soon as the product exits the interaction region. The ions were then accelerated via a four-electrode dc slice ion optics assembly to impact on a dual microchannel plate (MCP) detector coupled to a fast phosphor screen⁷. The detector was gated for the center slice of the scattered product ions and the resultant images were recorded using a charge-coupled device (CCD) camera and analyzed with our data acquisition program. Background subtraction and density-to-flux corrections were performed prior to transforming the scattering distributions in the center-of mass coordinate.

5.3 RESULTS

Crossed-molecular beam scattering with single photon ionization for many years has shown to be a sensitive technique to investigate bimolecular reactions. In probing the hydroxyalkyl radical using our 157 nm excimer laser, we need to take into account the detection efficiency for various radical products from the particular hydrogen abstraction sites. Both propanol isomers have two distinct abstraction sites: one at the hydroxyl end of the molecule and the other involving primary, secondary, and tertiary C-H groups.

Figure.5.1 Lowest energy structures of 1-propanol (left) and 2-propanol (right). Reaction enthalpies at 0 K (numbers in blue color, kcal mol⁻¹) at different abstraction sites are calculated at CBS-QB3 level of theory. Numbers in parenthesis are vertical ionization energies (eV) of corresponding product radicals.

Figure 5.1 presents the reaction enthalpies (0 K) for H abstraction by O (^3P) at the indicated sites, and the vertical ionization energies (eV) of corresponding product radicals (in parentheses).

The stationary point geometries for propanol isomers and their H abstraction radical products are optimized and their energies are calculated at the CBS-QB3 level of theory. Even though H abstractions from both hydroxyl group and C-H groups are energetically accessible according to the reaction enthalpies, the vertical ionization energy calculations indicate selectivity on the radical products that we can detect with our single photon ionization (7.9 eV). For 1-propanol, the ionization energy of the H abstraction product from the OH group and primary C-H group is higher than our detection probe of 7.9 eV, while the abstraction product from the secondary C-H group is lower. Thus, the radical products of the H abstraction on the α - and β -H sites are detected in the present work for 1-propanol. Analogously, for 2-propanol, we only detect the β -H abstraction radical product that is on the tertiary C-H group.

O (3P) + 1-propanol

Figure 5.5. Sliced scattering images for the reaction of O (3P) with 1-propanol (Newton diagrams superimposed on them) under collision energy of 8.1(left top panel) and 10.2 (left bottom panel) kcal mol $^{-1}$, and their corresponding global translational energy release ($P(E_T)$, right top panel) and center-of-mass angular ($T(\theta)$, right bottom panel) distributions. The $T(\theta)$ distributions are shown averaged every 10° with error bars ($\pm\sigma$) estimated by mean absolute deviation of the raw data in the corresponding angle range.

The reactive scattering images of the 1-hydroxypropyl radical products from the reaction of O(³P) with 1-Propanol at collision energies (E_c) of 8.1 and 10.2 kcal mol⁻¹ (with the Newton diagrams superimposed on them) are shown in the left panels of Figure 5.2. The 1-hydroxypropyl radical that we are probing here are produced from the H-abstraction from the α - and β -H sites of 1-propanol as we mentioned early. We performed background subtraction by recording images with the 193 nm photolysis laser off and the 157 nm probe laser on to isolate the reactive scattering signals from the radicals produced by the photodissociation of 1-propanol at 157 nm. Unfortunately, the intense photochemical signal creates substantial noise and brings uncertainty in the reactive flux of the forward component. For this reason, we omitted the first 45° of the forward component in the further analysis for this O(³P) + 1-propanol reaction. The right panels of Figure 2 show the corresponding global translational kinetic energy and center-of-mass angular distributions at two different collision energies (E_c = 8.1 kcal mol⁻¹ in black and E_c = 10.2 kcal mol⁻¹ in red). The average translational energy released at the collision energy of 10.2 kcal mol⁻¹ and 8.1 kcal mol⁻¹ is 5.3 and 3.5 kcal mol⁻¹, respectively. And the angular distributions at both collision energies show both sideways and backward scattering but preferential backward with respect to the direction of the propanol beam.

O (3P) + 2-propanol

Figure 5.6. Sliced scattering images for the reaction of O (3P) with 2-propanol under collision energy of 8.3 (left top panel) and 10.0 (left bottom panel) kcal mol $^{-1}$, and their corresponding global translational energy release ($P(E_T)$, right top panel) and center-of-mass angular ($T(\theta)$, right bottom panel) distributions. The $T(\theta)$ distributions are shown averaged every 10° with error bars ($\pm\sigma$) estimated by mean absolute deviation of the raw data in the corresponding angle range.

The left panels of Figure 5.3 show the sliced reactive scattering images of 2-hydroxypropyl radical products for the $\text{O} (^3\text{P}) + 2\text{-propanol}$ reaction at collision energy of 8.3 kcal mol⁻¹ (top) and 10.0 kcal mol⁻¹ (bottom). For this reaction, the 2-hydroxypropyl radical products that we probed here are only stemming from the H-abstraction from α -H sites of 2-propanol according to the ionization calculations. The total available energy for this reaction is 18.2 and 19.9 kcal mol⁻¹ for collision energy of 8.3 and 10.0 kcal mol⁻¹, respectively. Analogously to 1-propanol reaction, due to the large background interference in the forward direction, we have omitted the first 45° component in the further analysis for this $\text{O} (^3\text{P}) + 2\text{-propanol}$ reaction. The global translational energy release distributions are shown in the right top panel of Figure 5.3, with average translational energy of 4.2 and 5.4 kcal mol⁻¹ for the collision energy of 8.3 and 10.0 kcal mol⁻¹ accounting for 23% and 27% of the total available energy, respectively. The center-of-mass angular distributions of both collision energies are shown in the right bottom panel of Figure 5.3, indicating again more preferential backward scattering with respect to the propanol beam direction.

5.4 DISCUSSION

The reaction of ground state atomic oxygen with 1-propanol and 2-propanol has been studied with kinetic methods and the reaction rates of the H-abstraction from C-H group were measured.¹²⁰ The activation energy of both reactions was measure to be 12.5 and 9.1 kJ mol⁻¹ for 1-propanol and 2-propanol, respectively. 2-propanol has lower activation energy due to the weaker bond of its tertiary C-H group. No special steric effects were suggested in the reactions of the atomic oxygen with both propanol alcohols

from the kinetic measurement. The present work represents the further details of the underlying dynamics of the hydrogen abstraction for the oxygen atom $O(^3P)$ + propanol isomer reactions. The global differential cross sections as well as the translational energy partitioning were measured for the first time of these two reactions.

The angular distributions for both reactions under collision energies of 8 and 10 kcal mol⁻¹ show sideways-backward scattering and more favorable backward scattering is clearly observed, which implies direct rebound dynamics. Although we are not sensitive to the sharply forward-scattered products in the present work, we can rule out the forward-backward/isotropic symmetry that indicates the formation of complex during the reaction. This rebound dynamic involves small (but non-vanishing) impact parameter collisions, leading to direct reaction via a collinear transition state geometry, C-H-O, as suggested by the well-established line-of-centers model. Here, we refer to the collinear C-H-O coordinate as the line of center, not the line between the center-of-mass of the reactants.

The product translational energy release is also measured that gives important information about the dynamics. For both reactions, we re-plot the translational energy release distributions of the sideways (60°-120°) and backward (120°-180°) components against the collision energy as the reduced translational energy distributions (shown in Figure 5.4). For the collision energy of both 8 and 10 kcal mol⁻¹, the similar reduced translation energy distributions are presented in the SW and BW direction, indicating that the energy partitioning is not sensitive to the collision energy in the energy region of the present study. The detailed average translational energy of the SW/BW components and

the fraction of total energy (and collision energy) appearing in translation are summarized in Table 1. In both $\text{O}(^3\text{P}) + \text{propanol}$ reactions, the average translational energy release

Figure 5.7. Reduced translational energy distributions for sideways (SW) and backward (BW) scattering regions of the hydroxyalkyl products for low collision ($\sim 8 \text{ kcal mol}^{-1}$) and high collision ($\sim 10 \text{ kcal mol}^{-1}$) energy.

accounts for 20-30% of the total available energy and the energy partitioning increases with increasing collision energy. A simple way to view the dynamics of these reaction is an impulsive model that was widely used to understand photodissociation events.

Impulsive model assumes that the total available energy is released as an impulse along the breaking bond with momentum conservation between the two “atoms” governing the translational energy release. In this model, the fraction of translational energy is simply dependent upon the mass combination: $f_T = m_{ABC}m_B / (m_{AB}m_{BC})$ for dissociation of ABC, where C is bonded to (and recoils from) B, A remains initially as a spectator.¹²¹ This model predicts an f_T of 54% of the total available energy for the O (³P) + propanol systems, which is too high compared with experiment. Furthermore, this model cannot explain the collision energy dependence. The pure impulsive picture fails here since it assumes that all the energy is available for the partitioning between the fragments, which is unlikely if there is some internal excitation in recoiling fragments (*e.g.* hydroxyalkyl radical product) that does not relax completely during the OH-C bond breaking.

Another simple kinematic model for the linear triatomic system suggested by Evans et al. can also be used to predict the average translational energy release: $\langle E_T \rangle = E_c \cos^2 \beta + E_R \sin^2 \beta$, where β is the skew angle for the reaction, E_c is the collision energy, and E_R is the reaction energy. The skew angle is defined for A + BC by $\cos^2 \beta = (m_A m_B) / (m_{AB} m_{BC})$ and embodies key kinematics for the reaction. In this model, the remaining energy is allocated to vibrational excitation of the newly formed OH bond, therefore, it provides a rough limiting view to account for relaxation of the hydroxyalkyl

radical from the TS geometry. The OH radical generated from the titled reaction could be vibrationally excited given the experimental collision energy. In the previous LIF study of the O (^3P) + saturated alkane by Andresen and Luntz, OH radical was found to be rotationally cold regardless of the nature of the alkane reagent, but vibrational excitation of OH strongly depends on the type of hydrogen abstracted and increases dramatically across the series primary to secondary to tertiary. For the titled reactions, the skew angle is acute, as typically seen in heavy-light-heavy hydrogen transfer reactions, so the first term strongly dominates and predicts that the average translational energy is very close to the collision energy. This overestimate on the translational energy from this model suggests that the internal excitation in the hydroxyalkyl radical products plays an important role for the titled reactions.

A reasonable explanation for the internal excitation of the hydroxyalkyl radicals is the “vertical” abstraction mechanism that was invoked by Liu *et al.* in O + n-butane reaction and Whitney *et al.* in F + C₂H₆ reaction. In this picture, the C-H bond breaks so rapidly that hydroxypropyl radical cannot relax to its minimum energy geometry, resulting in a certain amount of energy “locked” in the C₃H₆OH moiety. This view is equivalent to the Franck-Condon picture that the hydrogen transfer is a “vertical” rather than an “adiabatic” process. Some available energy will be partitioned into vibrational excitation of the hydroxypropyl radical product in a non-statistical and mode-specific manner, associated with significant structural changes between propanol parent molecule and hydroxypropyl radical product. We have optimized the geometries of 1-propanol and 2-propanol and calculated the energy of hydroxypropyl moiety at this geometry at the CBS-QB3 level of theory. The minimum energy structures of the hydroxypropyl radical

products for each reaction were also optimized and their energy was calculated at the same level of theory. The energy difference between the vertical and adiabatic radical products from the H-abstraction is 8.2 kcal mol⁻¹ for 2-propanol, and 6.0 kcal mol⁻¹ or 7.3 kcal mol⁻¹ for 1-propanol with α -H or β -H abstraction. The major geometry changes accounting for this difference are summarized in Table 2. For instance, the C-C-C angle changes from $\sim 113^\circ$ to $\sim 121^\circ$ in both 2-propanol and 1-propanol by α -H abstraction. And the H-C-C-C dihedral angle changes from $\sim 122^\circ$ to $\sim 165^\circ$ in 1-propanol by β -H abstraction. These significant geometric changes as listed in Table 2.0 result in the corresponding vibrational excitation in the hydroxypropyl radicals, which could account for $\sim 50\%$ or more of the total available energy depending on the collision energy. We also expect that $\sim 20\%$ of the total available energy is partitioned to rotational excitation of hydroxypropyl radical product. The translational energy release is reduced in the sideway direction as shown in Table 1.0, indicating greater internal energy in the larger impact parameter collisions. This is consistent with greater rotational excitation for the sideway scattered products.

Apart from the O + n-butane reaction, another previous Cl + alcohol reactions studied by Ahmed et al. observed similar dynamics¹¹², i.e. dominant backward scattering and only $\sim 35\%$ - 40% of the total available energy partitioned to translation. We suspect a similar mechanism may account for the substantial internal excitation in the hydroxyalkyl product, although the details will need to be modified by the different relaxation energies and barriers, etc. With addition of present work, this “vertical” reaction mechanism seems to play an important role in H-abstraction dynamics in polyatomic systems.

5.5 CONCLUSION

We have performed an imaging study of the reaction dynamics of ground state atomic oxygen with propanol isomers under single collision conditions with well-defined collision energies of 8 and 10 kcal mol⁻¹. The hydroxypropyl radical products, generated from the α -H and β -H abstraction for 1-propanol and α -H abstraction for 2-propanol, were detected with our universal VUV (157 nm) soft ionization probe with velocity map imaging technique. The global differential cross sections and translational energy distributions were obtained from these images. Backward-sideways scattering but more favorable backward scattering was observed for both propanol isomer reactions under two different collision energy in the experiment. Low average translational energy release was obtained, accounting for 20%-30% of the total available energy, which indicates that a large amount of energy is released as the internal excitation of the products. As seen in the O + n-butane reaction, this can be explained by a modification of the triatomic model called as “vertical” H abstraction mechanism. In this picture, the H atom transfer is treated as a prompt “vertical” transition process, so that the hydroxypropyl radical does not have enough time to relax from the parent propanol geometry to the minimum energy geometry. This will lead to high internal excitation of the hydroxypropyl radical that is also supported by the *ab initio* calculations. This “vertical” reaction mechanism may play an important role in H-abstraction dynamics in more polyatomic systems.

Table 1.0 Summary of results on the translational energy partitioning for $O(^3P) + \text{propanol isomers}$

	E_C^a	E_{avl}^b	$\langle E_T \rangle$ SW^c	$\langle E_T \rangle$ BW^d	$\langle E_T \rangle / E_C$ SW^e	$\langle E_T \rangle / E_C$ BW^f	$\langle E_T \rangle / E_{avl}$ SW^g	$\langle E_T \rangle / E_{avl}$ BW^h
1-Propanol	8.1	15.9 ⁱ	3.25	3.81	0.41	0.48	0.20 ⁱ	0.24 ⁱ
		11.5 ^j					0.28 ⁱ	0.33 ^j
	10.2	18.0 ⁱ	4.75	5.3	0.46	0.51	0.26 ⁱ	0.29 ⁱ
		0.20 ^j					0.35 ^j	0.39 ^j
2-Propanol	8.3	18.2	3.51	4.26	0.42	0.51	0.19	0.23
	10.0	19.9	4.76	5.45	0.48	0.55	0.24	0.27

^aCollision energy. ^bTotal available energy (collision energy + reaction energy release). ^cAverage translational energy in the sideways direction. ^dAverage translational energy in the backward direction. ^eFraction of collision energy appearing in translation of the sideways component. ^fFraction of collision energy appearing in translation of the backward component. ^gFraction of total available energy appearing in translation of the sideways component. ^hFraction of total available energy appearing in translation of the backward component. ⁱResults from α -H abstraction site of 1-propanol. ^jResults from β -H abstraction site of 1-propanol.

Table 2.0 Results of *ab initio* calculations performed as described in the text
(hartrees, degrees, angstroms).

	CH ₃ CH ₂ CHOH	CH ₃ CH ₂ CHOH	CH ₃ CH ₂ CHOH	CH ₃ CH ₂ CHOH	(CH ₃) ₂ CHOH	(CH ₃) ₂ CHOH
Energy	-193.336314	-193.345812	-193.327093	-193.338695	-193.341587	-193.354680
∠OC1C2	108.0°	114.5°	—	—	—	—
∠C1C2C3	—	—	112.8°	121.4°	112.6°	121.4°
∠OC1C2C3	180.0°	170.8°	180°	166.6°	120.3°	143.1°
∠HC1C2C3	59.0°	-41.9°	-122.4°	-165.3°	—	—
O-C1/O-C2	1.427	1.375	—	—	1.439	1.383
C1-C2	1.521	1.488	1.521	1.484	1.526	1.495
C2-C3	—	—	1.531	1.489	1.525	1.490

*The radical structure at the geometry of its parent molecule. The lowest energy structure of the radical.
Bond length of O-C1 for CH₃CH₂CHOH and bond length of O-C2 for (CH₃)₂COH.

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VITA

Alexander Kamasah was born and grew up in Accra Ghana. He obtained his undergraduate degree from the university of Cape-Coast and relocated to the United States in the year 2010 for his M.Sc. degree (Analytical chemistry) at East Tennessee State University in Johnson City Tennessee. He then gained admission to Wayne State University in Detroit Michigan for his Ph.D. in physical chemistry, where He joined the Suits lab and studied crossed beam reaction dynamics. During the course of his Ph.D. program his supervisor relocated his lab to University of Missouri and he followed him to the university of Missouri. He completed his Ph.D. program in July 2018.