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Vibrational Spectra and Structural Parameters of Some XNCO (X=H, F, Cl, Br) Molecules

Abstract: *Ab initio* calculations with full electron correlation by the perturbation method to second order and hybrid density functional theory calculations by the B3LYP method utilizing the 6-31G(d), 6-311+G(d,p), and 6-311+G(2d,2p) basis sets have been carried out for the XNCO (X = H, F, Cl, Br) molecules. From these calculations, force constants, vibrational frequencies, infrared intensities, Raman activities, depolarization ratios, and structural parameters have been determined and compared to the experimental quantities when available. By combining previously reported rotational constants for HNCO, ClNCO and BrNCO with the *ab initio* MP2/6-311+G(d,p) predicted structural values, adjusted r_0 parameters have been obtained. The r_0 values for BrNCO are: $r(\text{Br}-\text{N}) = 1.857(5)$; $r(\text{N}=\text{C}) = 1.228(5)$; $r(\text{C}=\text{O}) = 1.161(5)$ Å; $\angle \text{BrNC} = 117.5(5)$ and $\angle \text{NCO} = 172.3(5)^\circ$. For ClNCO the determined r_0 parameters are in excellent agreement with the previously determined r_s values, whereas those for HNCO the HNC angle is larger with a value of $126.3(5)^\circ$ compared to the previous reported value of $123.9(17)^\circ$. However, considering the relatively large uncertainty in the value given initially the two results are in near agreement. Predicted values for the barriers of linearity are given for both the XNCO and XOCN (X = H, F, Cl, Br) molecules and the results were compared to the corresponding isothiocyanate molecules. The predicted frequencies for the fundamentals of the XNCO molecules compare favorably to the experimental values but some of the predicted intensities differ significantly from those in the observed spectra.

Keywords: *ab initio* calculations, infrared and Raman spectra, r_0 structural parameters, XNCO and XOCN (X = H, F, Cl, Br) molecules.

Introduction

Recently, several [1-6] spectroscopic studies supported by *ab initio* and density functional theory calculations of some YN_3 [1,2] and YNCS [3-6] molecules (Y = organic, silyl, germyl or halogen moiety) have been reported. Since the YNC angle is relatively large or in some cases linear, the NCS moiety has nearly free or free rotation which significantly affects the vibrational and rotational spectra. For example, the barrier to

internal rotation for methylisothiocyanate (CH_3NCS) is $\sim 3\text{ cm}^{-1}$ which results in essentially free rotation of the methyl group with the degeneracy of the two NCS bends [5]. In the infrared spectrum of the gas phase, two of the antisymmetric (pseudodegenerate) vibrations of the CH_3 groups have resolvable fine structure where the spacing is 9.8 cm^{-1} for the stretch and 13.8 cm^{-1} for the deformation where the spacing is determined by the zeta values for these normal modes for the CH_3NCS molecule [5]. Also the two NCS bends give a very strong broad infrared band in the gas and liquid along with a much weaker lower frequency band. In the infrared spectrum of the solid the very broad band essentially disappears leaving the single lower frequency band which may indicate a linear CNCS. This very low C-NCS torsional barrier for the methyl compound is also found for the corresponding ethyl compound [6] which results in a single stable *cis* conformer (CH_3 group *cis* to the NCS moiety) for this molecule which is at variance from the predictions from *ab initio* calculations up to TZVP [7]. Because of these large amplitude vibrations for these type of molecules, it has frequently been difficult to assign their microwave spectra from which rotational constants can be obtained for determining the r_0 or r_s structural parameters. However, it is frequently possible to combine a limited number of experimentally determined rotational constants with *ab initio* predicted structural parameters to obtain r_0 structural parameters that have significantly smaller uncertainties than those obtained from the microwave spectral data [8]. Such results have been obtained for HN_3 [1], CH_3N_3 [2], HNCS [3] and GeH_3NCS [5].

Since the $\angle\text{XNC}$ ($\text{X} = \text{H}, \text{CH}_3$) for the isocyanate is significantly smaller [9, 10] than the corresponding angles for the XNCS [3, 5] molecules, it is expected that the barrier to linearity will be much larger for the corresponding isocyanates. Also the $\text{N}=\text{C}$ distances may be significantly different between isocyanate and the corresponding isothiocyanate molecules. Therefore, as a continuation of these spectroscopic and theoretical investigations, a similar study of XNCO where $\text{X} = \text{H}, \text{F}, \text{Cl},$ and Br was carried out for comparison to the corresponding isothiocyanate (NCS) molecules. The results of these theoretical studies along with comparisons to the experimental data when appropriate are reported herein.

Theoretical Calculations

In order to provide vibrational frequencies with both infrared and Raman intensities and optimized geometries, *ab initio* calculations were carried out by using the Gaussian-98 program [11] at both the restricted Hartree-Fock (RHF) level and by the perturbation method to second order (MP2) [12] with full electron correlation. Three basis sets, 6-31G(d), 6-311+G(d) and 6-311+G(2d) have been utilized. Hybrid density functional theory (DFT) calculations have also been carried out by the B3LYP method utilizing the 6-311+G(d) basis set. Frequencies for the fundamentals have

been predicted for the XNCO (X = H, F, Cl, Br) molecules, along with the predicted infrared and Raman activities and these data are listed in Table 1. The predicted values are compared to the experimental values when they are available.

In order to obtain a complete description of the molecular motion involved in the normal modes, the force field in Cartesian coordinates was calculated with the 6-31G(d) and 6-311+G(d) basis sets at the MP2 level as well as with 6-311+G(d) basis set from the hybrid DFT calculations by B3LYP method. The internal coordinates were the X-N, N=C, and C=O distances, the XNC and NCO angle bends, and the out-of-plane angle bend for the isocyanates and X-O, O-C and C-N distances, the XOC and OCN bends, and the out-of-plane bend for the cyanates. The symmetry coordinates were these internal coordinates individually, except the C=O and N=C coordinates for antisymmetric and symmetric stretches was combined for the isocyanates. The **B** matrix was used to convert the *ab initio* force field in Cartesian coordinates to a force field in internal coordinates [13].

Table 1. Calculated^a frequencies (cm⁻¹) and potential energy distributions (PEDs) for XNCO (X = H, D, F, Br, Cl).

	ν	Description	IR Intensity ^b				
			MP2/6-31G(d)	MP2/6-311+G(d)	B3LYP/6-31G(d)	MP2/6-31G(d)	MP2/6-311+G(d)
HNCO							
A'	ν_1	N-H stretch	3732	3726	3733	169.6	166.3
	ν_2	NCO asym stretch	2376	2342	2316	506.3	676.8
	ν_3	NCO sym stretch	1316	1304	1293	0.4	0.05
	ν_4	HNC bend	779	768	811	266.3	215.1
	ν_5	NCO bend	567	562	577	81.9	101.6
A''	ν_6	NCO bend	618	627	633	0.8	0.5
DNCO							
A'	ν_1	N-D stretch	2762	2749	2726	205.7	201.4
	ν_2	NCO asym stretch	2346	2317	2312	453.6	629.0
	ν_3	NCO sym stretch	1297	1286	1318	0.8	1.4
	ν_4	DNC bend	694	698	703	82.4	61.8
	ν_5	NCO bend	471	458	457	108.2	109.2
A''	ν_6	NCO bend	602	611	621	8.8	6.8
FNCO							
A'	ν_1	NCO asym stretch	2257	2252	2253	344	438.7
	ν_2	NCO sym stretch	1287	1285	1308	0.4	1.2
	ν_3	N-F stretch	911	891	875	46.7	67.1
	ν_4	NCO bend	699	707	712	7.4	6.6
	ν_5	FNC bend	196	212	214	10.7	12.6
A''	ν_6	NCO bend	517	533	540	15.6	14.7
CINCO							
A'	ν_1	NCO asym stretch	2311	2296	2266	635.5	791.8
	ν_2	NCO sym stretch	1347	1340	1325	4.9	5.4
	ν_3	N-Cl stretch	702	706	694	30.2	29.1
	ν_4	NCO bend	611	615	617	2.3	1.4
	ν_5	CINC bend	166	163	153	12.1	11.9
A''	ν_6	NCO bend	540	558	564	20.0	17.1
BrNCO							
A'	ν_1	NCO asym stretch	2298	2285	2271	703.8	881.0
	ν_2	NCO sym stretch	1319	1317	1348	11.9	12.4
	ν_3	NCO bend	676	680	680	17.3	17.7
	ν_4	N-Br stretch	509	519	491	0.3	0.5
	ν_5	BrNC bend	135	136	136	6.5	6.8
A''	ν_6	NCO bend	550	565	577	17.2	15.5

^a For HNCS and DNCS the basis sets included p orbitals for the H and D atoms.

^b Calculated infrared intensities in km/mol.

^c Raman activities in Å⁴/u.

^d Frequencies for HNCO Ref. [24], DNCO [15], CINCO and BrNCO [30].

^e Frequencies for FNCO Ref. [26], BrNCO Ref. [35].

^f Calculated with MP2/6-31G(d) and contributions of less than 10% are omitted.

* Indication of misassignment in an earlier investigation [25].

B3LYP/6-31G(d)	Raman Activity ^a			Scaled	Obs		P.E.D. ^e
	MP2/6-31G(d)	MP2/6-311+G(d)	B3LYP/6-31G(d)		Gas ^d	Matrix ^a	
170.5	86.2	88.2	83.5	3540	3538.3		99S ₁
782.1	0.1	3.0	2.1	2254	2268.9		99S ₂
0.5	33.5	43.3	27.4	1316	1322.6		100S ₂
199.0	5.9	7.1	6.2	779	776.6		76S ₄ , 24S ₃
97.5	0.8	0.8	0.7	567	577.4		76S ₃ , 24S ₄
3.5	0.7	0.3	0.4	618	656.3		100S ₆
227.8	37.9	39.0	36.4	2620	2634.9		91S ₁
710.4	0.9	3.3	3.1	2226	2235.0		92S ₂
0.7	34.2	43.5	28.4	1297	1310.0		100S ₃
64.6	3.1	4.1	3.4	694	766.8		64S ₃ , 37S ₄
99.1	0.7	1.2	1.1	471	460.0		64S ₄ , 36S ₃
12.9	1.0	0.3	0.4	602	602.9		100S ₆
567.8	11.3	19.7	17.2	2141		2174.8	96S ₁
2.4	8.6	10.8	7.3	1221		1245.0	80S ₂ , 18S ₃
79.8	13.9	18.0	18.6	864		860.8	79S ₃ , 15S ₂
9.2	2.5	3.9	3.5	699		701.5	56S ₄ , 36S ₃
13.6	2.1	2.4	2.0	196		203.5*	67S ₃ , 35S ₄
20.7	0.7	0.2	0.3	517		533.8*	100S ₆
918.8	14.8	24.3	19.3	2192	2212.2		99S ₁
2.5	13.4	16.5	8.1	1278	1306.6		80S ₂ , 15S ₃
32.8	20.3	19.5	11.4	702	707.7		78S ₃ , 18S ₂
0.8	11.0	12.9	22.9	611	607.7		54S ₄ , 33S ₃
10.5	2.9	3.8	3.2	166	~230.0		67S ₃ , 36S ₄
23.7	0.5	0.1	0.1	540	559.0		100 ₆
1035.3	22.2	33.0	25.2	2180	2198.0	2196.0	99S ₁
6.6	14.8	18.9	8.6	1251	1294.5	1290.8	91S ₂
22.6	7.8	9.4	8.3	676	687.7	691.1	79S ₃ , 10S ₄ , 10S ₃
0.5	23.2	24.2	28.3	509	—	506.0	88S ₄ , 10S ₃
6.9	3.0	3.8	3.1	135	—	137.4	91S ₃ , 11S ₃
22.4	0.3	0.01	0.002	550	569.9	572.2	100S ₆

The frequencies from the MP2/6-31G(d) calculation were also calculated by utilizing a set of scaling factors of 0.88 for the N–H (N–D) stretches, 0.9 for HNC (DNC) bends, and 1.0 for all other coordinates with the geometric average for the off-diagonal terms for HNCO. Except for the acid, the potential energy distributions (P.E.D.s) are expressed in terms of the symmetry coordinates where: S_1 is NCO antisymmetric stretch, S_2 is the NCO symmetric stretch, S_3 is the X–N stretch, S_4 is the NCO bend, S_5 is the XNC bend and S_6 is out-of-plane bend; these potential energy distributions are listed in Table 1. For the acid, S_1 is N–H (N–D) stretch, S_2 is NCO antisymmetric stretch, S_3 is the NCO symmetric stretch, S_4 is HNC (DNC) bend, S_5 is NCO bend and S_6 is the out-of-plane bend. The pure *ab initio* frequencies, infrared intensities, Raman scattering activities, along with the B3LYP/6-311+G(d) calculation results are also given in Table 1.

In order to show the differences in the predicted and observed spectra for the fluoro-, chloro- and bromoisocyanates as well as the difference in the infrared and Raman spectra for the hydrogen and halocyanates, we calculated the theoretical infrared and Raman spectra. The calculated frequencies, infrared intensities, and Raman scattering activities were obtained from both the *ab initio* and hybrid DFT calculations. Infrared intensities were calculated based on the dipole moment derivatives with respect to the Cartesian coordinates. The derivatives were taken from the *ab initio* calculation and transformed to the normal coordinates by $(\partial\mu_u/\partial Q_i)=[\sum(\partial\mu_u/\partial X_j)]L_{ji}$, where Q_i is the i^{th} Cartesian displacement coordinate, L_{ji} is the transformation matrix between the Cartesian displacement coordinates and normal coordinates. The infrared intensities were then calculated by: $I_i = [(N\pi)/(3c^2)] [(\partial\mu_x/\partial Q_i)^2+(\partial\mu_y/\partial Q_i)^2+(\partial\mu_z/\partial Q_i)^2]$.

For HNCO and DNCO, mainly the predicted infrared and Raman spectra are shown in Figure 1. In Figs. 2–4, the predicted infrared spectra from the MP2(full)/6-31G(d) calculations are shown for each XNCO (X = F, Cl, Br) molecule. For comparison the experimental infrared spectra of the gas or in a matrix are also shown. The observed ones show some slight differences from the predicted ones for these molecules. An analytical gradient method has been developed [14, 15] for the evaluation of the Raman activity. Where the activity, S_j , can be expressed as: $S_j = g_j (45\alpha_j^2 + 7\beta_j^2)$ and g_j is the degeneracy of the vibrational mode j , α_j is the derivative of the isotropic polarizability, and β_j is that of the anisotropic polarizability. The Raman scattering cross sections, which are proportional to the Raman intensities, can be calculated from the scattering activities [16,17]. To obtain the polarized Raman cross sections, the polarizabilities are incorporated into S_j by multiplying S_j with $(1-\rho_j)/(1+\rho_j)$, where ρ_j is the depolarization ratio of the j^{th} normal mode. The

Raman scattering cross sections and the calculated frequencies were used together with the Lorentzian function to obtain the calculated spectrum. The predicted Raman spectrum for the individual molecules is shown below the infrared spectrum, but only the experimental one for BrNCO is conveniently available for comparison.

Vibrational Spectra and Structural Parameters

The predicted vibrational spectra for the XNCO ($X = \text{H, D, F, Cl, Br}$) molecules are shown in Figs. 1–4 and it should be noted that in general there are significant differences in the predicted intensities of the lower frequency bending modes of the infrared spectra and those in the Raman spectra. For example, with BrNCO, the ν_4 fundamental is barely observable in the infrared spectrum but it is the strongest Raman band. Similarly the ν_6 mode is extremely weak in the Raman spectrum but the third strongest band in the infrared spectrum. Some similar differences are also predicted for the other XNCO molecules ($X = \text{F and Cl}$). Thus, these data could be of significant importance for any future Raman studies of the other halocyanates. However, infrared and Raman data as well as experimental structural data are available for isocyanic acid.

3.1 Isocyanic acid (HNCO and DNCO)

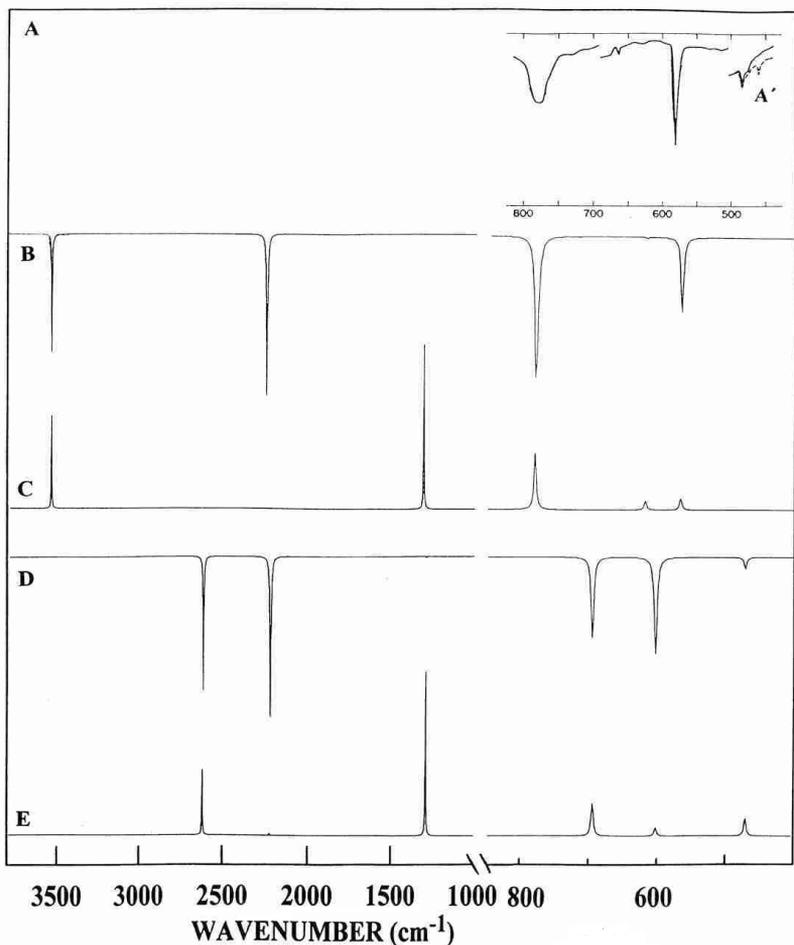


Fig. 1 Vibrational spectra of HNCO and DNCO: (A) experimental (Ref. [38]) infrared spectrum of HNCO in nitrogen matrix; and (A') HOCN spectrum generated from HNCO; (B) simulated infrared and (C) Raman spectra of HNCO from MP2/6-31G(d) calculation; (D) simulated infrared and (E) Raman spectra of DNCO from MP2/6-31G(d) calculation. Note scale changes.

The predicted infrared spectrum of HNCO from scaled MP2/6-31G(d) calculations is shown in Fig. 1B and that for DNCO in 1D, and the corresponding Raman spectra are shown in 1C and 1E, respectively. The predicted intensities for ν_2 in the Raman spectra makes them almost unobservable compared to the other Raman line intensities whereas the corresponding symmetric NCO stretch (ν_3) is the most intense Raman line with the corresponding infrared band extremely weak as might be expected from a comparison of these corresponding modes of CO_2 . Because of this exceedingly small intensity, this mode was misassigned in the early infrared investigation [18] with a frequency of 1527 cm^{-1} . The question concerning the correct assignment for ν_3 should not have occurred since this mode was clearly observed by Goubeau [19] in the Raman spectrum. The predicted Raman intensity of this fundamental is the second highest (Table 1), and is only exceeded by the predicted intensity of the NH stretch and the only other fundamental with significantly predicted Raman intensity is the HNC bend. There was also some controversy concerning the assignment for the HNC bend (ν_4) as well as the out-of-plane NCO bend (ν_6, A''). For example, ν_6 was assigned at 777.1 cm^{-1} [20] which was later supported by *ab initio* SCF calculations [21] that was in agreement with earlier CNDO/2 calculations [22]. However, the higher level calculations (Table 1) clearly show that the out-of-plane mode is the band at 656.3 cm^{-1} , but again the intensity is extremely small which undoubtedly contributed to the earlier misassignment.

The potential energy distributions for ν_4 and ν_5 for HNCO and DNCO are rather interesting where, for the deuterium compound, there is 64% contribution of the NCO bend (S_5) to the higher frequency band at 767 cm^{-1} whereas for the hydrogen compound the corresponding band at 777 cm^{-1} is 76% HNC bend (S_4). The halocyanate NCO bend is heavily mixed with the XNC bend for the fluoro- and chloro- compounds as well as with the X-N stretches. However, this mixing is relatively small for the bromide. Therefore the simple descriptions of the three bands below the symmetric NCO stretch for the haloisocyanates do not give a very good indication of the atom displacements for these modes.

TABLE 2. Structural parameters,^a rotational constants, dipole moments and energies for HNCO.

Parameter	RHF/6-311+G(d,p)	MP2/6-31G(d)	MP2/6-311+G(d,p)	B3LYP/6-311+G(d,p)	Microwave		Adjusted r_0
					[23]	[9] ^c	
r(H-N)	0.994	1.009	1.007	1.006	0.986	0.995(6)	0.995(3)
r(N=C)	1.197	1.224	1.224	1.212	1.209	1.214(3)	1.216(3)
r(C=O)	1.139	1.184	1.172	1.166	1.166	1.166(1)	1.165(3)
\angle HNC	124.3	125.8	123.2	126.2	128.0	123.9(17)	126.1(5)
\angle NCO	174.4	171.1	171.6	172.8	(180) ^b	172.6(27)	172.6(5)
A	876,748	884,244	827,323	903,406	912,712	918,504	918,423
B	11,483	10,816	10,951	11,078	11,071	11,071	11,057
C	11,335	10,686	10,808	10,944	10,910	10,910	10,925
$ \mu_a $	1.544	1.857	1.700	1.690	1.575(5)		
$ \mu_b $	1.681	1.767	1.767	1.523	1.35(10)		
$ \mu_c $	0.0	0.0	0.0	0.0	0.0		
$ \mu_d $	2.282	2.563	2.452	2.275	2.07(10)		
-(E+167)	0.814554	1.232429	1.368556	1.738737			

^a Bond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energies in Hartree.

^b Assumed.

^c Modified substitution method

The structural parameters for HNCO have been obtained from two microwave studies [9, 23] with relatively low uncertainties for the distances but with larger uncertainties for the HNC and NCO angles of $123.9 \pm 1.7^\circ$ and $172.6 \pm 2.7^\circ$, respectively (Table 2). In the initial microwave study [23], NCO was assumed to be linear with a relatively large \angle HNC of 128.0° and a very short N=C distance of 1.209 Å. Later the microwave data was reanalyzed by using a modified substitution method along with a nonlinear NCO which resulted in more reasonable angles but with relatively large uncertainties. We have combined the *ab initio* predicted parameters from the MP2/6-311+G(d,p) calculations along with the previously reported rotational constants [23] from the following isotopes ^{15}N , ^{13}C , ^{18}O , and D as well as with the normal species to obtain the five structural parameters. The values we obtained for the HNC angle is $126.1 \pm 0.5^\circ$, and $172.6 \pm 0.5^\circ$ for the NCO angle, both of which are nearly in agreement with the values previously reported but with smaller uncertainties. Also it should be noted that the values obtained from the *ab initio* MP2/6-311+G(d,p) calculations as well as those from the B3LYP/6-311+G(d,p) calculations are in reasonable agreement with the experimental values but different from the theoretical values previously reported [24] with the smaller 6-31G(d,p) basis set.

3.2 Fluorine Isocyanate (FNCO)

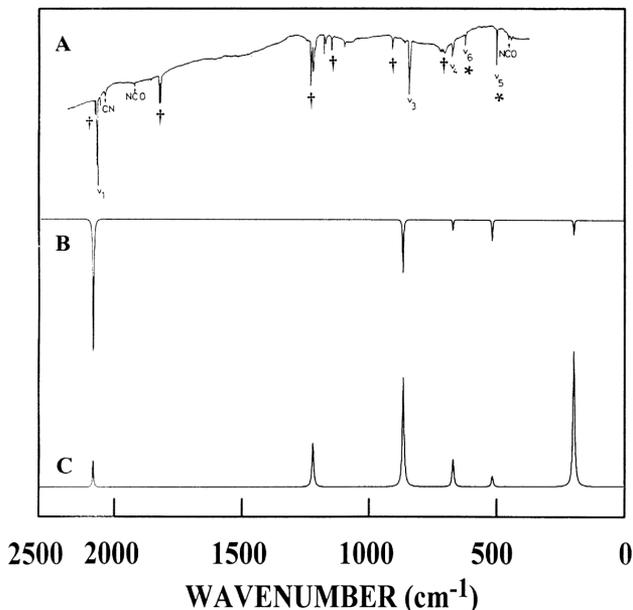


Fig. 2 Vibrational spectra of FNCO: (A) experimental infrared spectrum (Ref. [25]) from argon matrix obtained by UV photolysis of $\text{FC}(\text{O})\text{N}_3$; † spectrum of precursor; * the original assignment of ν_6 , later reassign to ν_5 band; simulated spectra from MP2/6-31G(d) calculation (B) infrared and (C) Raman.

The initial infrared spectrum of FNCO was reported by Gholi-vand et al. [25] from an argon matrix where the sample was generated by UV-photolysis of $\text{FC}(\text{O})\text{N}_3$ and five of the six fundamentals were assigned (Fig 2). The NCO symmetric stretch (ν_2) was not assigned but as can be seen from the *ab initio* predicted spectrum this fundamental is predicted to be very weak (Fig. 2B) as might be expected from the similar mass for the oxygen and nitrogen atoms and their electronegativities. The predicted frequency is expected to be the lower limit since this mode is predicted too low for all of the other XNCO molecules investigated herein. Initially there were two modes (ν_5, ν_6) which were misassigned with the weak band at 646 cm^{-1} (Fig. 2A marked with an asterisk) assigned as ν_6 but it is obvious that this band is not a fundamental. The band at 529 cm^{-1} which was previously assigned [25] as ν_5 is in fact ν_6 , the out-of-plane NCO mode, and ν_5 is predicted to have a frequency of 196 cm^{-1} which was

beyond the range of their spectroscopic investigation at the time. Later in a reinvestigation [26] of the infrared spectrum of FNCO including ^{15}N , ^{13}C , and ^{18}O isotopic species by utilizing a neon matrix, ν_5 was observed at 203.5 cm^{-1} and ν_6 reassigned to the band at 533.8 cm^{-1} (Table 1).

The predicted intensities for the four observed fundamentals shown in Fig. 2 agree very well with the observed values. It is probable that the predicted intensities for the Raman lines would also agree well with the Raman data if the spectrum were recorded. Finally the extensive mixing of two of the A' modes should be noted. Therefore, to refer to one of them as the FNC bend (Table 1) is an over simplification since this mode is extensively mixed with the NCO bend. A similar problem is also found for the in-plane NCO bend of the corresponding chlorine molecule.

TABLE 3. Structural parameters,^a rotational constants, dipole moments and energies for FNCO.

Parameter	RHF/6-311+G(d)	MP2/6-31G(d)	MP2/6-311+G(d)	B3LYP/6-311+G(d)	Adjusted r_0
$r(\text{F-N})$	1.361	1.418	1.403	1.409	1.406(5)
$r(\text{N=C})$	1.233	1.262	1.258	1.246	1.248(5)
$r(\text{C=O})$	1.127	1.176	1.166	1.157	1.158(5)
$\angle\text{FNC}$	111.0	110.7	112.0	112.6	112.6(5)
$\angle\text{NCO}$	173.5	168.9	169.1	169.8	169.8(5)
A	59087	58268	61291	61592	61479
B	5312	4901	4917	4944	4947
C	4874	4520	4552	4577	4579
$ \mu_a $	0.978	0.740	0.876	0.806	
$ \mu_b $	0.376	0.412	0.411	0.344	
$ \mu_c $	0.0	0.0	0.0	0.0	
$ \mu_t $	1.048	0.847	0.968	0.876	
$-(E+266)$	0.571179	1.144187	1.350977	1.898154	

^aBond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energies in Hartree.

No structural studies have been reported for FNCO so it was not possible to obtain adjusted r_0 parameters from the *ab initio* predicted values but we have some estimated r_0 parameters (Table 3). To determine the expected quality of the NF distance we have carried out some *ab initio* calculations on some other NF containing molecules: $\text{F}_2\text{C=NF}$, HNF_2 , and CH_3NF_2 where the NF distances have been experimentally determined [27, 28, 29, respectively]. The predicted NF distances were compared to those experimentally determined by the same basis sets and level of calculations used to predict the parameters for FNCO. For

F₂C=NF the MP2(full)/6-311+G(d) calculations predicted the NF distance within 0.002 Å which was the listed uncertainty of the experimental determination. For the HNF₂ molecule the predicted distance was too short by 0.009 Å but the B3LYP calculation with the same basis set gave a predicted NF distance of 0.003 Å. A similar results was obtained for the CH₃NF₂ molecule.

Therefore, we believe the NF distance for FNCO should be somewhere between the predicted value of 1.403 Å for FNCO from the MP2 calculations (Table 3) and 1.409 Å from the B3LYP calculations, *i.e.* 1.406 Å.

3.3 Chlorine Isocyanate (ClNCO)

The infrared spectrum of gaseous ClNCO has been reported [30] and five of the fundamentals were assigned from observed bands with the low frequency ClNC bend (ν_5) estimated at ~ 230 cm⁻¹ from combination and difference bands (Table 1). However as can be seen from the predicted frequency of 166 cm⁻¹ for this fundamental, this estimated frequency is entirely too high. Based on the predicted frequencies for the FNC and BrNC bending modes compared to the observed values it is expected that the ClNC bend should be within the estimated value of 166 ± 4 cm⁻¹. The predicted frequencies for the other fundamentals have errors similar to those found for the corresponding vibrations for the FNCO molecule.

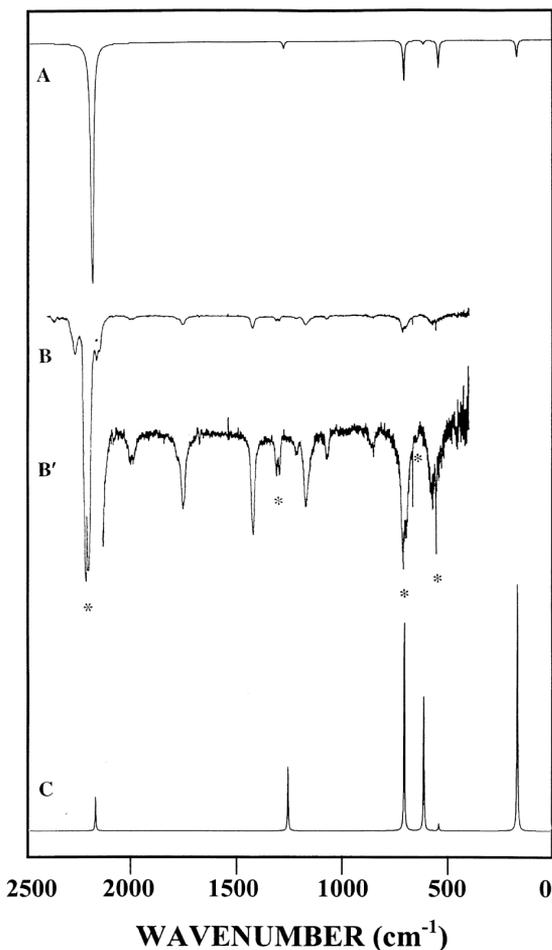


Fig. 3 Vibrational spectra of ClNCO: (A) simulated infrared spectrum from MP2/6-31G(d) calculation; (B) experimental infrared spectrum of the gas (Ref. [30]); (B') an expansion of the weaker bands by five times; * indicating the observed fundamentals; (C) simulated Raman spectrum from MP2/6-31G(d) calculation.

The predicted intensities of the infrared bands agrees very well with the experimentally observed values (Fig. 3) where the ν_4 mode is predicted to be quite weak and ν_1 very, very strong. The ν_6 fundamental is predicted to be quite weak in the Raman spectrum but there is no experimental data for comparison. These predicted intensities for the infrared and Raman spectra do not differ significantly among the three

different calculations (Table 1).

There have been two microwave studies of CINCO where in the first investigation [31] only three isotopic species (^{35}Cl , ^{37}Cl , ^{18}O) were studied so only a partial substitution structure was obtained which necessitated the use of one of the principal moments. This resulted in a rather large variation in the bond lengths and angles depending on the moment used to obtain the distance so the accuracy of the determined parameters was quite low (Table 4). However in the second microwave study [32], three more isotopic species were investigated which included ^{15}N with ^{35}Cl and ^{37}Cl and ^{13}C with ^{35}Cl so sufficient spectral data were obtained with all of the atoms substituted. A complete substitution structure was obtained and the determined parameters are listed in Table 4. The listed uncertainties are relatively small so these results were used to evaluate the quality of the adjusted r_0 parameters obtained from the *ab initio* predicted parameters adjusted to fit the microwave rotational constants. These data show the use of the *ab initio* predicted values coupled with the microwave rotational constants provide excellent values for the structural parameters.

TABLE 4. Structural parameters,^a rotational constants, dipole moments and energies for CINCO

Parameter	RHF/6-311+G(d)	MP2/6-31G(d)	MP2/6-311+G(d)	B3LYP/6-311+G(d)	MW ^b (r_0)	Adjusted r_0
$r(\text{Cl-N})$	1.697	1.709	1.708	1.730	1.705(5)	1.706(5)
$r(\text{N=C})$	1.212	1.241	1.236	1.227	1.226(5)	1.225(5)
$r(\text{C=O})$	1.132	1.181	1.170	1.162	1.162(5)	1.162(5)
$\angle\text{CINC}$	119.5	121.9	121.1	120.8	118.8(3)	118.9(5)
$\angle\text{NCO}$	174.4	169.6	170.3	171.4	170.9(3)	171.0(5)
A	50448	57763	55781	53570	51576	51571
B	3219	2978	3027	3035	3131	3127
C	3026	2832	2871	2872	2945	2948
$ t_a $	0.371	0.807	0.799	0.603		
$ t_b $	0.779	0.845	0.775	0.631		
$ t_c $	0.0	0.0	0.0	0.0		
$ t_d $	0.863	1.168	1.113	0.873		
-(E+626)	0.6663709	1.211139	1.408280	2.299173		

^a Bond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energies in Hartree.

^b Ref. [32].

3.4 Bromine Isocyanate (BrNCO)

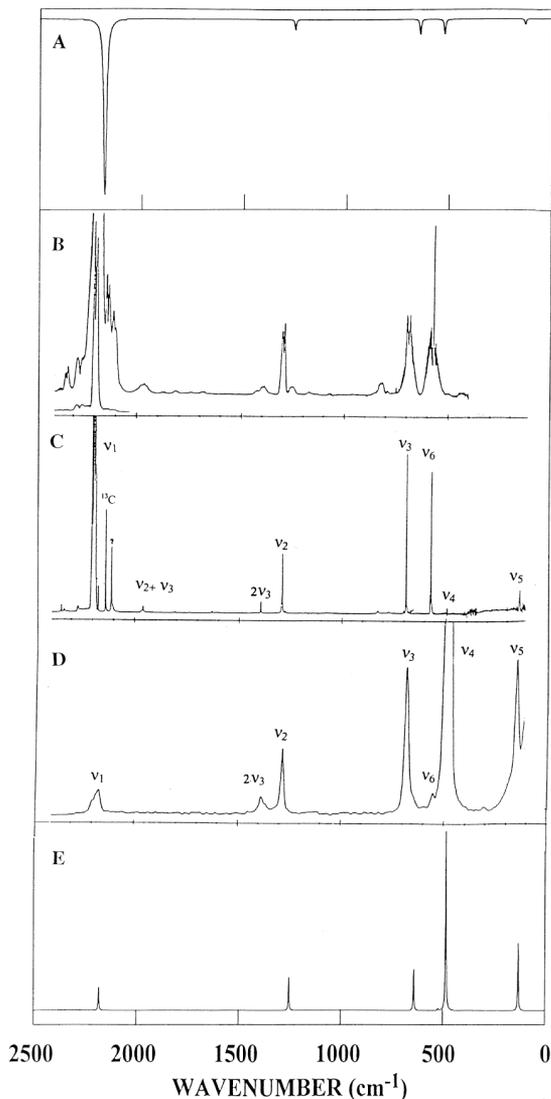


Fig. 4 Vibrational spectra of BrNCO: (A) simulated infrared spectra from MP2/6-31G(d) calculation; experimental (Ref. [35]) (B) infrared spectrum of the gas (resolution: 1 cm^{-1}), (C) infrared spectrum in neon matrix (resolution: 0.5 cm^{-1}), (D) Raman spectrum of the liquid (resolution: 4 cm^{-1}); and (E) simulated Raman spectra from MP2/6-31G(d) calculation.

The infrared spectrum for BrNCO was initially reported [33, 34] with only about one-half of the observed bands assigned. A more extensive study of the infrared spectrum of the gas was reported [30] with frequencies given for four of the fundamentals and six other bands assigned with four of them as combination bands and two as difference modes. This study was followed by an in-depth vibrational investigation [35] which included Raman spectrum of the liquid, infrared spectrum of the gas and matrix-isolated (Ne and Ar) of the normal species and Ar matrices for ^{15}N , ^{13}C , and ^{18}O enriched species. Some of these spectral data are shown in Fig. 4 along with the *ab initio* predicted infrared and Raman spectra. Remarkably good agreement is found between the observed and predicted spectra of both the infrared and Raman data. From these data the final two fundamentals were confidently assigned (Table 1). There were some very large differences between the frequencies in the neon matrix and those from the liquid, i.e. 137 g (150 l); 506 g (490 l); 572 g (560 l); 2196 g (2168 l). These differences indicate significant association in the liquid phase.

TABLE 5. Structural parameters,^a rotational constants, dipole moments and energies for BrNCO.

Parameter	RHF/6-311+G(d)	MP2/6-31G(d)	MP2/6-311+G(d)	B3LYP/6-311+G(d)	MW ^b (r_i)	Adjusted r_i
r(Cl-N)	1.697	1.709	1.708	1.730	1.705(5)	1.706(5)
r(N=C)	1.212	1.241	1.236	1.227	1.226(5)	1.225(5)
r(C=O)	1.132	1.181	1.170	1.162	1.162(5)	1.162(5)
$\angle\text{CNC}$	119.5	121.9	121.1	120.8	118.8(3)	118.9(5)
$\angle\text{NCO}$	174.4	169.6	170.3	171.4	170.9(3)	171.0(5)
A	50448	57763	55781	53570	51576	51571
B	3219	2978	3027	3035	3131	3127
C	3026	2832	2871	2872	2945	2948
$ u_a $	0.371	0.807	0.799	0.603		
$ u_b $	0.779	0.845	0.775	0.631		
$ u_c $	0.0	0.0	0.0	0.0		
$ u_d $	0.863	1.168	1.113	0.873		
-(E+626)	0.6663709	1.211139	1.408280	2.299173		

^a Bond distances in Å, bond angles in degrees, rotational constants in MHz, dipole moments in Debye and energies in Hartree.

^b Ref. [37].

^c Initial microwave studies [36] show that the parameters has been deduced from limited isotopic data, only rBr-N, $\angle\text{BrNC}$ and $\angle\text{NCO}$ were varied.

There have been two microwave studies of BrNCO where in the first one only two isotopomers were investigated (^{79}Br and ^{81}Br) and three parameters were varied $r(\text{Br-N})$, $\angle\text{BNC}$ and $\angle\text{NCO}$ with the other parameters assumed to be the same as the corresponding parameters of the ClNCO molecules [36]. In the later microwave study [37] the ^{18}O isotopomers (^{79}Br and ^{81}Br) were investigated and with the rotational constants of the four isotopomers both r_0 and r_z structural parameters were determined (Table 5). Both of these results gave a rather short NC distance compared to the value obtained in this study by combining the *ab initio* predicted parameters with the “fit” of the microwave rotational constants (Table 5). The *ab initio* predicted parameters for the NCO moiety are nearly the same for the chlorine and bromine cyanate which is a strong indication that the relatively large difference suggested from the microwave data alone are probably in error.

Discussion

It is clear that the NCO moiety is bent in the ground vibrational state from both the microwave data and the *ab initio* predicted parameters.

Calculation level	HNCO Ground State (Hartree)	NCO linearity (cm^{-1})	molecular linearity (cm^{-1})	FNCO Ground State (Hartree)	NCO linearity (cm^{-1})
RHF/6-311+G(d,p) ^c	-167.814554	222	1332	-266.577300	220
MP2/6-31G(d)	-168.232430	385	1643	-267.144186	450
MP2/6-311+G(d,p) ^c	-168.368556	396	1725	-267.350977	446
MP2/6-311+G(2d,2p) ^c	-168.41116	373	1969	-267.416678	417
B3LYP/6-311+G(d,p) ^c	-168.738737	302	1422	-267.898154	421

TABLE 6. Calculated barriers to NCO moiety linearity^a and barriers to molecular linearity^b of XNCO (X = H, F, Cl and Br) molecules.

^a NCO moiety linearity is defined with NCO group assuming $C_{\infty v}$ point group, and with XNCO molecules assuming C_s point group.

^b Molecular linearity is defined with XNCO molecules assuming $C_{\infty v}$ point group.

^c The second designation in parentheses, *p*-orbital polarization functions, only apply to the hydrogen atom in HNCO.

The linearity of the NCO moiety for all of the XNCO (X = H, F, Cl, Br) molecules was calculated (Table 6) and the values are very similar for all four molecules. The predicted values for the HNCO molecule range from a low 222 cm⁻¹ (RHF/6-311+G(d,p)) value to the high value of 396 cm⁻¹ (MP2(full)/6-311+G(d,p)) with an average value of 335 cm⁻¹ from the five different calculations. A similar average value is found for the BrNCO molecule with the other two molecules having values of 390 cm⁻¹. These values on average are ~130 cm⁻¹ larger than the barriers to linearity of the NCS moiety for the similar molecules [3]. The barriers to molecular linearity of the XNCS (X = H, F, Cl, Br) molecules are somewhat smaller (~1000 cm⁻¹ average) than the corresponding ones for the XNCO (X = H, F, Cl, Br) molecules. Also it should be noted that the barrier to molecular linearity of FNCO is about five times larger than the value for HNCO and about three times larger than those for the other two halides (Table 6). The larger barriers to molecular linearity for the XNCO molecules are undoubtedly due to the significantly small \angle XNC angle of the cyanates compare to the similar angle of the isothiocyanates.

molecular linearity (cm ⁻¹)	CINCO Ground State (Hartree)	NCO linearity (cm ⁻¹)	molecular linearity (cm ⁻¹)	BrNCO Ground State (Hartree)	NCO linearity (cm ⁻¹)	molecular linearity (cm ⁻¹)
8292	-626.672232	204	2769	-2739.547696	174	2361
8553	-627.211139	502	3033	-2737.630255	431	3205
8373	-627.408280	456	3128	-2740.614637	388	3106
8083	-627.481774	421	2758	-2740.672012	376	2355
7890	-628.299173	366	2933	-2742.233645	313	2763

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