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Experimental and Theoretical Vibrational Studies of Covalent X−N$_3$ Azides (X = H, F, Cl, Br, I). Application of the Density Functional Theory and Comparison with ab Initio Results[†]

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The infrared spectra of gaseous chlorine azide, bromine azide and iodine azide as well as the Raman spectrum of liquid chlorine azide were recorded. The geometries and vibrational spectra of all halogen azides XN$_3$ (X = F, Cl, Br, I) and HN$_3$ were computed employing density functional theory calculations (DFT) at the self-consistent level with the nonlocal exchange functional of Becke (B) and the nonlocal correlation functional of Lee−Yang−Parr (B-LYP). The results were compared with those previously reported by Frenking et al. (Inorg. Chem. **1992,** *31,* 3647−3655) using quantum chemical ab initio methods at the Hartree−Fock and correlated levels. The results of DFT calculations and *experimentally obtained* vibrational spectra indicate that the ν(X−N$_3$) stretching modes (X = Cl, Br, I) had previously been assigned incorrectly. The general agreement between the computed geometries at correlated levels (ab initio, MP2; DFT, B-LYP) and the observed structures is very good. Whereas the ab initio calculations predict too high frequencies due to the neglect of electron correlation and of anharmonicity and require scaling, the DFT computations at the correlated level (B-LYP) predict for all covalent azides considered the vibrational modes remarkably well and no scaling was required.

Introduction

The chemistry of HN$_3$ and its halogen derivatives XN$_3$ (X = F, Cl, Br, I) is fascinating and presents many mysteries.[1] Thus, IN$_3$ exists like all other halogen azides in a trans-bent (C_s) structure in the gas phase, is monomeric in CFCl$_3$ solution[2] but forms a chain-like polymer in the crystalline state.[1,3] It was only in recent years that the molecular structures of the heavier halogen azides BrN$_3$ and IN$_3$ were determined experimentally.[1,3,4] This recent resurgence of halogen azide chemistry has also stimulated theoretical work on this subject. For example, quantum mechanical ab initio studies of the structures and stabilities of halogen azides have been reported.[5] In this respect, the trans-bent (C_s) geometries of all isolated X−N$_3$ halogen azides have extensively been discussed on the basis of localized molecular orbitals from the natural bond orbital (NBO) viewpoint.[1] Moreover, the vibrational spectra of the halogen azides XN$_3$ (X = F, Cl, Br, I) and HN$_3$ have been calculated by quantum chemical ab initio methods.[5] For the heavier halogen azides, however, there is still a considerable degree of confusion concerning the assignment of the ν(X−N$_3$) stretching modes.[1a]

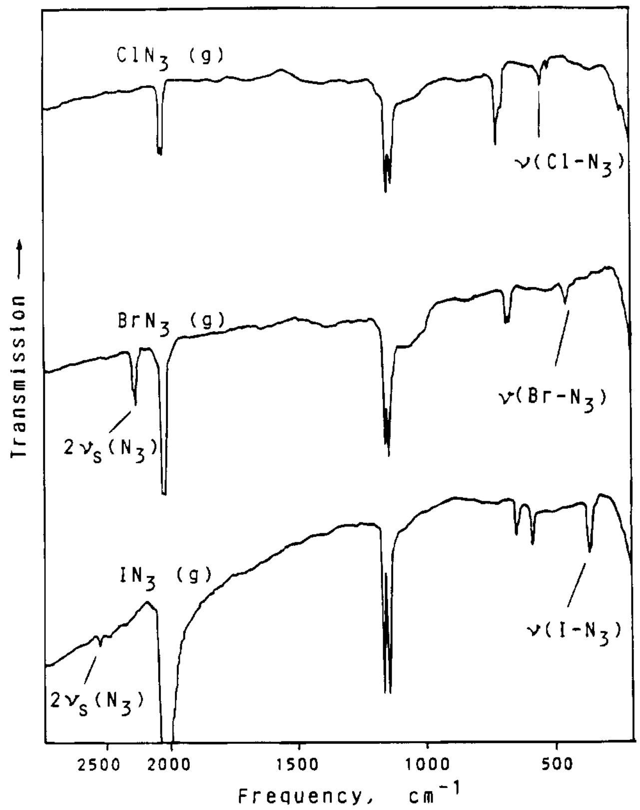

Figure 1. Infrared spectra of gaseous ClN$_3$, BrN$_3$, and IN$_3$.

In recent studies the quality of density functional calculations for relatively large and heavy halogen containing molecules was tested. It has been established that usually the calculated vibrational frequencies are in excellent agreement with the experimental values.[6] Therefore, we decided to reinvestigate the halogen azides XN$_3$ (X = F, Cl, Br, I) and HN$_3$ employing

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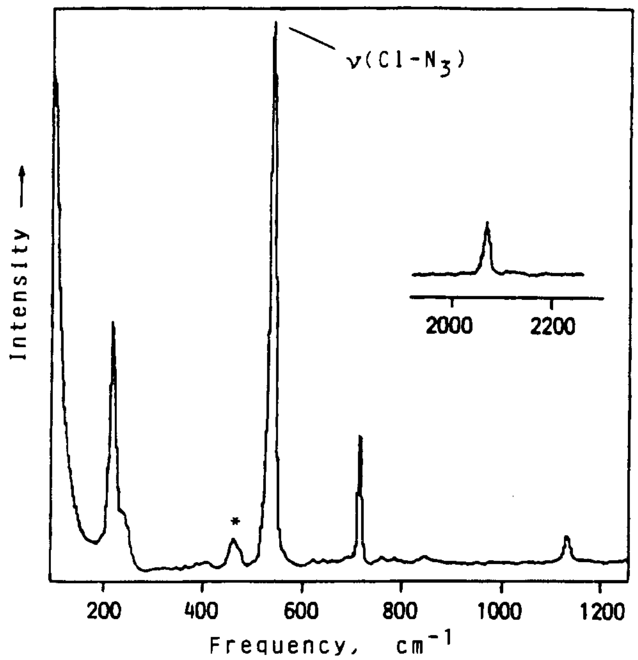

Figure 2. Raman spectrum of liquid ClN$_3$ (647 nm, 50 mW, −50 °C, * = impurity)

density functional theory and reassigned the ν(X−N$_3$) stretching modes for ClN$_3$, BrN$_3$ and IN$_3$.

Experimental Section

Caution! Covalent azides are generally highly explosive; covalent and ionic azides are very toxic and appropriate safety precausions should be taken.

Materials. The syntheses of the halogen azides have been previously described. Chlorine azide, ClN$_3$, was prepared from NO$_2$Cl and Me$_3$SiN$_3$;[7] bromine azide was obtained from neat NaN$_3$ and elemental bromine;[4] iodine azide was synthesized from silver azide and iodine in CFCl$_3$ solution.[3]

Vibrational Spectroscopy. Infrared spectra were recorded at 20 °C by using a 10 cm gas cell (2 Torr) equiped with CsI windows on a Perkin-Elmer Model 580 B spectrophotometer.

Raman spectra were recorded on a Jobin Yvon Ramanor U 1000 spectrophotometer using the 547-nm exciting line of a Kr ion laser. Thin-walled 5-mm Pyrex glass tubes were used as sample containers.

Computational Methods. The geometries and vibrational spectra described below were calculated by using the density functional theory[8] with the program package Gaussian 92/DFT.[9] For H, N and F a 6-31+G* basis set was used, for Cl, Br and I quasi-relativistic pseudopotentials and the DZ+P basis set was used.[10] The density functional computations were done at the density functional level with the local Slater exchange functional[11] extended by the nonlocal exchange functional of Becke (B).[12] Correlation was taken into consideration by using the nonlocal correlation functional of Lee−Yang−Parr (B-LYP).[13]

Results and Discussion

The objective of this work was to undoubtedly establish or to reassign the X−N$_3$ stretching modes of the heavier halogen

Table 1. Computed and Experimentally Observed Geometries and Total Energies of the Halogen Azides and HN$_3$ (Distances in Å; Angles in deg; E_{tot} in hartrees)

X−N1−N2−N3; X = H, F, Cl, B, I	HF/LANL1DZ+P[5]	MP2/LANL1DZ+P[5]	B/6-31+G* [a]	BLYP/6-31+G* [a]	exptl data[b]
		HN$_3$			
r(X−N1)	1.006	1.023	1.045	1.032	1.015
r(N1−N2)	1.247	1.266	1.278	1.256	1.243
r(N2−N3)	1.102	1.171	1.167	1.156	1.134
∠(N1N2N3)	174.3	171.5	169.1	169.9	171.3
∠(XN1N2)	107.8	109.0	109.4	110.5	108.8
$-E_{tot}$	163.8707	164.3699	164.0105	164.7734	
		FN$_3$			
r(X−N1)	1.383	1.441	1.518	1.474	1.444
r(N1−N2)	1.263	1.293	1.295	1.273	1.253
r(N2−N3)	1.103	1.161	1.169	1.158	1.132
∠(N1N2N3)	174.7	172.4	169.7	169.9	170.9
∠(XN1N2)	104.2	103.3	104.1	104.8	103.8
$-E_{tot}$	262.6606	263.3103	262.8624	263.9410	
		ClN$_3$			
r(X−N1)	1.742	1.767	1.900	1.840	1.745
r(N1−N2)	1.257	1.278	1.284	1.264	1.252
r(N2−N3)	1.102	1.167	1.170	1.159	1.133
∠(N1N2N3)	174.7	171.7	169.6	170.2	171.9
∠(XN1N2)	108.3	108.1	108.2	108.9	108.6
$-E_{tot}$	177.9528	178.5733	178.1675	179.1011	
		BrN$_3$			
r(X−N1)	1.891	1.919	2.040	1.977	1.90
r(N1−N2)	1.251	1.274	1.279	1.260	1.23
r(N2−N3)	1.103	1.170	1.172	1.160	1.13
∠(N1N2N3)	174.8	171.9	169.6	170.3	171
∠(XN1N2)	109.8	109.4	109.5	110.1	110
$-E_{tot}$	176.1829	176.7946	176.5707	177.4881	
		IN$_3$			
r(X−N1)	2.058	2.095	2.247	2.182	2.14
r(N1−N2)	1.245	1.268	1.272	1.254	1.26
r(N2−N3)	1.104	1.175	1.174	1.162	1.14
∠(N1N2N3)	174.8	171.8	169.1	170.0	168
∠(XN1N2)	112.3	111.2	111.8	112.3	107
$-E_{tot}$	174.4187	175.0188	174.6254	175.5257	

[a] Effective core potentials for Cl, Br, I: [5s5p1d]/(3s3p1d)-DZ+P). [b] Microwave data for HN$_3$,[23] FN$_3$ [14] and ClN$_3$.[24] Electron diffraction data for BrN$_3$ [4] and IN$_3$.[3] Experimental uncertainties: Δr ≤ 0.02 Å, Δ∠ ≤ 1.0°.

Table 2. Average Deviations of ab Initio and DFT Computed Structural Parameters of the Halogen Azides and HN_3 from the Experimentally Observed Data

	HF/LAN-L1DZ+P[5]	MP2/LAN-L1DZ+P[5]	B/6-31+G*[a]	BLYP/6-31+G*[a]
Δr (Å)	0.03	0.03	0.06	0.03
$\Delta\angle$ (deg)	2.8	1.5	1.5	1.5

[a] Effective core potentials for Cl, Br, I: [5s5p1d]/(3s3p1d)-DZ+P).

azides X−N_3 (X = Cl, Br, I). Vibrational data of all halogen azides have been reported previously, and the X−N_3 stretching modes were assigned as follows: ν(F−N_3) = 873 cm^{-1},[14] ν(Cl−N_3) = 719 cm^{-1},[15] ν(Br−N_3) = 687 cm^{-1},[16] and ν(I−N_3) = 410[17] or 338 cm^{-1}.[18] For IN_3 different assignments have been made, and a recent theoretical study[5] on this subject supported the assignment of Engelhardt et al. at 410 cm^{-1}.[17] The azide group can be considered as a pseudohalogen in the way that it has the property of existing as a monomeric univalent anion and in many ways displays properties analogous to single halogen atoms.[19] Moreover, the group electronegativity (χ) of the N_3 radical was calculated using the equation $\chi = (I + A)/2$ (I, ionization energy; A, electron affinity) and was shown to lie between the value for Cl and that for Br ($\chi = (I + A)/2$: Cl, 8.3; N_3, 7.7; Br, 7.5 eV).[20] Therefore, it would be interesting to compare the ν(X−N_3) stretching frequencies with those observed for the interhalogen compounds X−Cl (X = F, Cl, Br, I) and X−Br: ν(F−Cl) = 793 cm^{-1}, ν(Cl−Cl) = 546 cm^{-1}, ν(Br−Cl) = 443 cm^{-1} and ν(I−Cl) = 384 cm^{-1}; ν(F−Br) = 671 cm^{-1}, ν(Br−Br) = 319 cm^{-1}, and ν(I−Br) = 265 cm^{-1}.[21] In this respect, the assignment of the ν(F−N_3) mode at 873 cm^{-1} seems to be correct. However, the X−N_3 stretching modes of ClN_3 and BrN_3 appear at far too high wavenumbers, and in the case of IN_3 the old assignment at 338 cm^{-1} would compare much better with the simple pseudohalogen principle. Moreover, if one compares the Cl−N_3 stretching mode with the *symmetrical* N−Cl stretching mode observed for NCl_3 (535 cm^{-1})[22] the value of 719 cm^{-1} reported for ClN_3 again seems to be too high and it is likely that this vibration had been assigned incorrectly. (N.b. NCl_3: ν_{sym} = 535 cm^{-1}, A_1; ν_{asym} = 637 cm^{-1}, E; $\bar{n} = (A_1 + 2E)/3$ = 603 cm^{-1}. The value of 603 cm^{-1} is much closer to 545 cm^{-1} than to 719 cm^{-1}.) Therefore, we reinvestigated the vibrational spectra of the heavier halogen azides and recorded the gas phase infrared spectra of ClN_3, BrN_3, and IN_3 (Figure 1). Since the band corresponding to the new assigned Cl−N_3 stretching mode appeared rather weak in the IR spectrum, ClN_3 was also studied in the liquid state by low-temperature Raman spectroscopy (Figure 2). The geometries and vibrational spectra of these species and in addition of FN_3 and HN_3 were computed by using density functional theory.

Table 1 summarizes the computed and experimentally observed geometries and total energies of the halogen azides and HN_3. The results from previous ab initio calculations at

Table 3. Experimentally Observed and Calculated Vibrational Frequencies from Different Methods at Different Levels of Theory for XN_3 Species (X = H, F, Cl, Br, I) (Wavenumbers in cm^{-1}; Computed IR Intensities in km mol^{-1})

azide	HF/LANL1DZ+P[5]	MP2/LANL1DZ+P[5]	B/6-31+G*[a]	B-LYP/6-31+G*[a]	exptl IR[b]	exptl Raman[c]	assignt
X−N_3 Stretching Mode							
HN_3	3681 (29)	3573 (68)	3221 (13)	3354 (27)	3324 (m)		ν(H−N)
FN_3	1029 (210)	928 (51)	753 (72)	812 (87)	873 (s)		ν(F−NNN)
ClN_3	816 (45)	761 (8)	455 (2)	474 (9)	545 (mw)	542 (s)	ν(Cl−NNN)
BrN_3	769 (23)	708 (4)	357 (7)	400 (5)	452 (m)		ν(Br−NNN)
IN_3	471 (<1)	426 (<1)	322 (3)	358 (2)	360 (m)	410 (vs)?	ν(I−NNN)
Asymmetrical N_3 Stretching Mode							
HN_3	2298 (489)	2350 (203)	2066 (282)	2163 (305)	2150 (vs)		ν_a(HNNN)
FN_3	2354 (409)	2384 (155)	1940 (125)	2037 (136)	2037 (vs)		ν_a(NNN)
ClN_3	2415 (555)	2359 (278)	1944 (202)	2048 (228)	2075 (s)	2074 (w)	ν_a(NNN)
BrN_3	2418 (657)	2330 (369)	1936 (224)	2044 (256)	2058 (vs)		ν_a(NNN)
IN_3	2423 (814)	2291 (483)	1926 (269)	2037 (309)	2055 (vvs)	2052 (m)	ν_a(NNN)
Symmetrical N_3 Stretching Mode							
HN_3	1055 (296)	1135 (190)	1091 (144)	1139 (193)	1168 (vs)		ν_s(HNNN)
FN_3	1266 (30)	1135 (2)	1011 (9)	1095 (7)	1090 (m)		ν_s(NNN)
ClN_3	1202 (165)	1173 (25)	1060 (30)	1143 (29)	1145 (s)	1136 (w)	ν_s(NNN)
BrN_3	1228 (232)	1190 (37)	1079 (36)	1160 (36)	1150 (s)		ν_s(NNN)
IN_3	1267 (306)	1209 (46)	1107 (45)	1186 (46)	1170 (s)	1207 (w)	ν_s(NNN)
Deformation Mode, Out-of-Plane							
HN_3	584 (1)	559 (1)	541 (6)	564 (4)	588 (w)		γ(HNNN)
FN_3	599 (9)	470 (2)	436 (2)	456 (2)	504 (w)		γ(NNN)
ClN_3	616 (11)	484 (2)	424 (12)	475 (3)	522 (w)	*d*	γ(NNN)
BrN_3	627 (11)	480 (<1)	465 (2)	485 (3)	*d*		γ(NNN)
IN_3	640 (11)	500 (2)	475 (2)	497 (3)	578 (m)	583 (w)	γ(NNN)
Deformation Mode, In-Plane							
HN_3	1422 (76)	1237 (3)	1230 (54)	1250 (11)	1273 (m)		δ(HNNN)
FN_3	748 (6)	673 (5)	574 (17)	616 (10)	658 (m)		δ(FNNN)
ClN_3	615 (8)	570 (1)	642 (19)	670 (23)	719 (m)	719 (m)	δ(ClNNN)
BrN_3	520 (3)	493 (2)	622 (14)	644 (16)	682 (m)		δ(NNN)
IN_3	743 (16)	676 (4)	607 (13)	626 (14)	648 (m)	628 (vw)	δ(NNN)
Deformation Mode, In-Plane							
HN_3	506 (17)	541 (29)	483 (14)	504 (15)	527 (w)		δ(HNNN)
FN_3	283 (5)	245 (5)	211 (3)	220 (4)	241 (m)		δ(FNNN)
ClN_3	246 (2)	209 (3)	190 (1)	197 (2)	223 (sh)	223 (m)	δ(ClNNN)
BrN_3	213 (<1)	178 (2)	167 (<1)	174 (1)	*d*		δ(BrNNN)
IN_3	194 (1)	161 (2)	153 (<1)	158 (1)	*d*	218 (w)	δ(INNN)

[a] Effective core potentials for Cl, Br, I: [5s5p1d]/(3s3p1d)-DZ+P). [b] IR data: HN_3,[25] FN_3.[14] ClN_3, BrN_3, and IN_3, this work; see also, ClN_3,[15] BrN_3,[16] and IN_3.[5] [c] Raman data: ClN_3, this work and ref 7; IN_3, ref 17. [d] Not observed.

HF and correlated MP2 levels have also been included. Table 2 shows the average differences between the experimentally observed and computed structural parameters for the halogen azides. Usually, ab initio HF calculations give too short bond distances whereas DFT computations always seem to predict somewhat too long distances. It can be concluded that the uncorrelated ab initio (HF) and the DFT (B) calculations are of similar quality. The density functional computation usually gives better bond angles but the HF method results in better distances and vice versa. On correlated levels both methods, ab initio (MP2) and density functional theory (B-LYP), compare nicely with the experimental data.

The calculated vibrational frequencies from different methods at different levels of theory are given in Table 3 together with the experimentally observed data. In all cases the frequencies obtained from DFT computations are better in agreement with the experimental values. Since the basis sets and pseudo potentials used for the ab initio calculations (Frenking et al.: LANL1DZ+P) and those used for the DFT computations (this work: 6-31+G*; effective core potentials for Cl, Br, I: [5s5p1d]/(3s3p1d)-DZ+P) are of comparable quality it can be stated that DFT computations generally predict better frequencies than ab initio calculations do (cf. ref 6). As the accuracy of the computed harmonic frequencies corresponds to the calculated potential energy curves it can be assumed that density functional theory reflects the shape of the potential energy curves better than ab initio calculations do. Therefore, in the present study the B-LYP frequencies seem to be most reliable. Table 4 summarizes the average deviations of the ab initio and DFT computed frequencies of the halogen azides and HN_3 from the experimentally observed data.

Table 4. Average Deviations of the ab Initio and DFT Computed Frequencies of the Halogen Azides and HN_3 from the Experimentally Observed Data

	HF/LANL1DZ+P^5	MP2/LANL1DZ+P^5	B/6-31+G*^{a}	B-LYP/6-31+G*^{a}
$\Delta\nu$ (cm^{-1})	135	83	78	29

[a] Effective core potentials for Cl, Br, I: [5s5p1d]/(3s3p1d)-DZ+P).

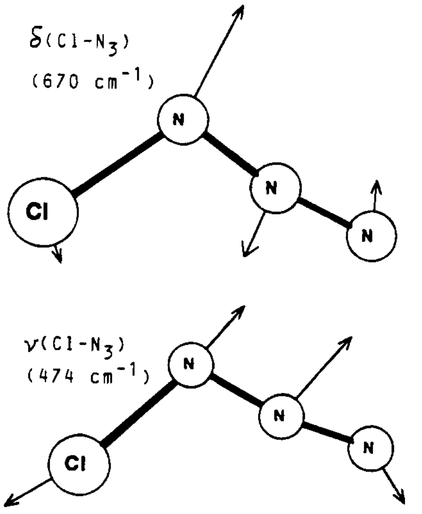

Figure 3. Normal modes in ClN_3: $\nu(X-N_3)$, 474 cm^{-1} (B-LYP); $\delta(XN_3)$, 670 cm^{-1} (B-LYP).

The careful interpretation of the experimentally obtained and DFT computed vibrational frequencies at correlated level (B-LYP) unambiguously indicates that the $X-N_3$ stretching modes should be assigned as follows: $\nu(F-N_3) = 873$ cm^{-1}, $\nu(Cl-N_3) = 545$ cm^{-1}, $\nu(Br-N_3) = 452$ cm^{-1}, and $\nu(I-N_3) = 340$ cm^{-1}. Therefore, these modes had previously been assigned incorrectly for the azides ClN_3 and BrN_3. In the case of IN_3 we support the earlier assignment of Dehnicke et al. at 340 cm^{-1}. It is quite obvious that in the case of ClN_3 and BrN_3 the $\nu(X-N_3)$ and the $\delta(XN_3)$ had been interchanged. Figure 3 shows the representation of these two vibrations for chlorine azide. BrN_3 and IN_3 possess $X-N_3$ vibrational modes that are qualitatively identical with that of ClN_3 shown in Figure 3.

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