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An ab Initio Study of Anharmonicity and Field Effects in Hydrogen-Bonded Complexes of the Deuterated Analogues of HCl and HBr with NH_3 and $N(CH_3)_3$

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One- and two-dimensional nuclear Schrödinger equations have been solved on MP2/aug′-cc-pVDZ potential energy surfaces generated for ClH:NH_3 and ClH:$N(CH_3)_3$ and on MP2/6-31+G(d,p) surfaces generated for BrH:NH_3 and BrH:$N(CH_3)_3$ to investigate deuterium substituent effects on the expectation values of X−N and X−H distances and on anharmonic dimer- and proton-stretching frequencies. These studies have been carried out on all isotopomers in the presence of electric fields of varying strengths. Deuteration of HX or ammonia or trimethylamine has only minor effects on expectation values and dimer-stretching frequencies. While deuteration of the nitrogen base also has only a minor effect on proton-stretching frequencies, deuteration of the hydrogen halide has a major effect, as expected. X−D stretching frequencies are always lower than the corresponding X−H frequencies at all field strengths, although the ratio $\nu(D)/\nu(H)$ for corresponding pairs of isotopomers may be less than, equal to, or greater than the harmonic ratio of 0.71. Structural and vibrational spectral changes as a function of field strength are similar for a given complex and each of its isotopomers. The agreement between computed proton-stretching frequencies and experimental frequencies supports the validity of this approach for modeling matrix effects on the structures and vibrational spectra of hydrogen-bonded complexes. The computed results provide insight into the nature of the hydrogen bonds that stabilize these complexes in low-temperature matrixes.

Introduction

In previous papers we have investigated the structures and vibrational spectra of a variety of hydrogen-bonded complexes.[1−4] The hydrogen bonds in these complexes may be classified as one of three types: traditional; proton-shared; ion pair. In a complex with a traditional A−H···B hydrogen bond, the A−H distance is slightly elongated relative to the monomer A−H distance, and the B−H distance is significantly longer than a normal B−H covalent distance. If proton transfer from A to B occurs within the complex, an ion-pair hydrogen bond is formed. In such a complex the B−H distance is slightly elongated relative to the B−H distance in the corresponding ion, and the A−H distance is longer than a normal covalent bond distance. Complexes with traditional hydrogen bonds are associated with IR spectra characterized by a single intense A−H stretching band shifted to lower frequency relative to the monomer, while complexes with ion-pair hydrogen bonds exhibit a strong B−H stretching band shifted to lower frequency relative to the corresponding cation. Intermediate between traditional and ion-pair hydrogen bonds are proton-shared A···H···B hydrogen bonds. In this type of hydrogen bond, the A−H and B−H distances are longer than the corresponding monomer distances, but the A−B distance is shorter than the A−B distance in traditional and ion-pair hydrogen bonds. Complexes with proton-shared hydrogen bonds are characterized by potential surfaces that are very anharmonic, and multiple strong low-frequency bands associated with the proton-stretching vibration may be found in the IR spectra.[1−4,5−8] Recent work has demonstrated that strong correlations exist among the structure of a hydrogen-bonded complex, the IR proton-stretching frequency, and the NMR properties of the chemical shift of the hydrogen-bonded proton and the A−B spin−spin coupling constant across the A−H−B hydrogen bond.[9−11]

In a recent paper[4] we investigated hydrogen bonds in complexes of HCl and HBr with NH_3 and $N(CH_3)_3$ and demonstrated how these complexes may be stabilized in the presence of isotropic electric fields. Typically, experimental vibrational spectroscopic data for hydrogen-bonded complexes are obtained using low-temperature matrix-isolation techniques. Comparison of spectra obtained in different matrices indicates that the matrix material does influence the IR spectrum of a complex.[12−14] We have used isotropic external electric fields as a simple model for a matrix environment.[4] The values chosen for the external field strengths are consistent with Onsager's reaction field model for dipolar fluids.[15,16] Although a simplification, this approach provided insight into the nature and mechanism by which interaction between the complex and a matrix occurs and an explanation for the apparently disparate effects of Ar and N_2 matrixes on the spectra of related complexes.[4]

An electric field preferentially stabilizes the more polar hydrogen-bonded structures. Depending on the acid and base strengths of the proton-donor and proton-acceptor species, the hydrogen bond at zero field may exhibit traditional, proton-shared, or ion-pair character. If traditional, and if the proton-shared region of configuration space is energetically accessible,

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an increasing external field will serve to increase the proton-shared character of the hydrogen bond, with a resultant lowering of the proton-stretching vibrational frequency. The proton-stretching frequency is minimum at the quasi-symmetric proton-shared structure, and the forces on H from A and B are equal.[4,8] Further increasing the field leads to the formation of an ion-pair hydrogen bond and an increase in the proton-stretching frequency. If the hydrogen bond at zero field is a proton-shared or ion-pair hydrogen bond, imposing relatively small external fields leads to an increase in ion-pair character, and the proton-stretching frequency increases with increasing field strength.

In this paper we extend our original study of the complexes of HCl and HBr with NH_3 and $N(CH_3)_3$ to the deuterated analogues of these complexes. Although the electronic potential surfaces for the normal and corresponding deuterated complexes are the same, the deuterated species lie lower in the potential wells, so that the relative anharmonicities and behavior of A−D−B hydrogen bonds in electric fields will be different from A−H−B. Moreover, detailed analysis of the trends in the IR frequencies in a series of deuterated complexes provides a stringent test of our theoretical methods and may provide clues for the assignment of the experimentally observed spectra. In this paper we report the dependence of the structures and proton-stretching vibrational frequencies of the deuterated complexes on external electric fields of varying strengths and, where possible, compare these frequencies with experimental frequencies obtained in argon and nitrogen matrices.

Methods

The proton-stretching vibrations of the hydrogen-bonded complexes $ClH{:}NH_3$, $BrH{:}NH_3$, $ClH{:}N(CH_3)_3$, and $BrH{:}N(CH_3)_3$ are significantly anharmonic.[1,2,4] To obtain acceptable agreement between computed and experimental proton-stretching frequencies for these complexes, it is necessary to calculate, at a minimum, two-dimensional anharmonic vibrational wave functions and energies. These calculations involve solving the Schrödinger equation for nuclear motion on appropriate two-dimensional potential energy surfaces. The methods used to generate and characterize the potential surfaces for $ClH{:}NH_3$, $BrH{:}NH_3$, $ClH{:}N(CH_3)_3$, and $BrH{:}N(CH_3)_3$ and to solve the two-dimensional nuclear Schrödinger equation for these complexes have previously been described in detail[4,17] and will be summarized briefly here.

Two-dimensional grids of ab initio single-point energies for complexes constrained to C_{3v} symmetry were generated by freezing the ammonia or trimethylamine coordinates and varying the N−H and X−H distances. Results at nonzero field strengths were obtained similarly by applying an external field along the X−H−N direction and varying the N−H and X−H distances. In this way a discrete grid of ab initio data at second-order many-body Møller−Plesset perturbation theory (MP2)[18−21] was obtained for each complex. Electronic energies for complexes with HBr were computed using the 6-31+G(d,p) basis set,[22−25] while complexes with HCl were investigated using the Dunning correlation-consistent polarized valence double-split basis set augmented with diffuse s, p, and d functions on non-hydrogen atoms (aug′-cc-pVDZ).[26−28] All calculations were performed by freezing the s and p electrons below the valence shells in the Hartree−Fock molecular orbitals. These methods have been used previously to study hydrogen-bonded complexes and have been shown to produce reliable structures and shifts of the proton-stretching frequency relative to the monomer if the anharmonicity correction is not large.[29,30] In addition, studies of small complexes for which the anharmonicity correction is large indicate that this level of theory provides results which are comparable to those obtained from more sophisticated calculations.[2,3]

TABLE 1: Dipole Moment, Cavity Radius, and Onsager Reaction Field for the Equilibrium Geometry of $ClH{:}NH_3$ and the Traditional (T) and Proton-Shared (PS) Structures of $BrH{:}NH_3$ and $ClH{:}N(CH_3)_3$ and $BrH{:}N(CH_3)_3$ at $\epsilon = 1.6$ and 2.0[a]

species	dipole moment (D)	cavity radius (bohr)	reacn field	
			$\epsilon = 1.6$	$\epsilon = 2.0$
$ClH{:}NH_3$	4.71	6.17	0.0023	0.0032
$BrH{:}NH_3$ (T)	4.79	6.60	0.0019	0.0026
$BrH{:}NH_3$ (PS)	8.40	6.36	0.0037	0.0052
$ClH{:}N(CH_3)_3$	8.49	7.77	0.0020	0.0028
$BrH{:}N(CH_3)_3$	9.71	7.94	0.0022	0.0031

[a] There were errors in the data reported in ref 4, Table 6, for $ClH{:}NH_3$ and $BrH{:}NH_3$. The corrected numbers are given above.

Global potential energy surfaces and one- and two-dimensional anharmonic vibrational eigenfunctions and eigenvalues were calculated as previously.[4] The sensitivity of the calculated frequencies to the procedure used to generate the surfaces is estimated to be less than 6 and 7 cm^{-1} for the dimer- and proton-stretching frequencies, respectively. Within the Born−Oppenheimer approximation, the potential energy surfaces are identical for a given complex and all of its deuterated analogues. The mass effects of deuteration are manifest only from the solution of the vibrational Schrödinger equation.

All calculations reported here were carried out on the Cray T94 computer at the Ohio Supercomputer Center and on the computing facilities at the University of Sydney. Gaussian 98[33] was used to generate the ab initio data points for the potential energy surfaces without and with electric fields.

Results and Discussion

Table 1 presents reaction field strengths for $ClH{:}NH_3$, $BrH{:}NH_3$, $ClH{:}N(CH_3)_3$, and $BrH{:}N(CH_3)_3$ in dielectrics with relative permittivities of 1.6 (solid Ar at 10 K)[34] and 2.0 (to illustrate solid N_2).[35] The dipole moments of $ClH{:}N(CH_3)_3$ and $BrH{:}N(CH_3)_3$ are larger than the dipole moments of the equilibrium structures of $ClH{:}NH_3$ and $BrH{:}NH_3$, but complexes with trimethylamine are larger and have larger cavity radii than complexes with ammonia. Thus, the ensuing reaction fields are comparable. The fields strengths that were chosen are 0.0010, 0.0025, 0.0040, 0.0055, 0.0100, and 0.0150 au for $ClH{:}NH_3$; 0.0005, 0.0010, 0.0025, 0.0040, 0.0080, and 0.0120 au for $BrH{:}NH_3$; and 0.0010 and 0.0040 au for $ClH{:}N(CH_3)_3$ and $BrH{:}N(CH_3)_3$.

$ClH{:}NH_3$, $ClH{:}ND_3$, $ClD{:}NH_3$, and $ClD{:}ND_3$. The equilibrium Cl−H and Cl−N bond lengths and the expectation values of the Cl−H and Cl−N distances taken from ref 4 for $ClH{:}NH_3$ at various field strengths are reported in Table 2, along with the corresponding data for the deuterated complexes. The proton- and dimer-stretching frequencies are reported in Table 3.

We begin by summarizing the most important features of $ClH{:}NH_3$, which were reported in ref 4. The zero-field equilibrium structure of $ClH{:}NH_3$ is stabilized by a traditional hydrogen bond. The H−Cl distance (R_e) of 1.341 Å is only slightly longer than that of the HCl monomer, 1.288 Å, indicating that proton transfer to N does not occur. The intermolecular Cl−N distance (R_e) is 3.080 Å. This structure is in agreement with the experimental microwave structure reported by Legon.[36] The proton-stretching motion in this complex may be described as a perturbed Cl−H stretch. As external electric fields of increasing strengths are applied, the minimum on the

TABLE 2: Equilibrium (R_e) and Expectation Values (R_0) in the Ground Vibrational State for the Cl−N (R) and Cl−H (R_2) Distances (Å) in ClH:NH$_3$ and Its Deuterated Analogues

field	R_e	R_{2e}	ClH:NH$_3$[a] R_0	ClH:NH$_3$[a] R_{20}	ClH:ND$_3$ R_0	ClH:ND$_3$ R_{20}	ClD:NH$_3$ R_0	ClD:NH$_3$ R_{20}	ClD:ND$_3$ R_0	ClD:ND$_3$ R_{20}
0.0000	3.080	1.341	3.016	1.392	3.016	1.393	3.041	1.374	3.040	1.374
0.0010	3.056	1.349	2.986	1.411	2.984	1.411	3.011	1.389	3.011	1.389
0.0025	3.019	1.363	2.941	1.448	2.939	1.449	2.960	1.421	2.958	1.421
0.0040	2.975	1.383	2.905	1.495	2.904	1.496	2.909	1.473	2.908	1.474
0.0055	2.832	1.575	2.870	1.546	2.884	1.546	2.878	1.538	2.877	1.539
0.0100	2.896	1.766	2.898	1.692	2.898	1.692	2.895	1.710	2.895	1.710
0.0150	3.004	1.917	2.988	1.857	2.987	1.856	2.996	1.878	2.995	1.878

[a] Data taken from ref 4.

TABLE 3: Harmonic and Anharmonic Proton and Dimer Stretching Frequencies (cm^{-1}) as a Function of Field Strength (au) for ClH:NH$_3$ and Its Deuterated Analogues

	harmonic: "triatomic" surface		anharmonic			
			dimer		proton	
field	dimer	proton	1-D	2-D	1-D	2-D
ClH:NH$_3$[a]						
0.0000	189	2278	193	202	1905	1567
0.0010	185	2191	193	213	1740	1415
0.0025	220	2054	198	244	1388	1219
0.0040	220	1787	208	301	972	1067
0.0055	440	507	362	372	1039	936
0.0100	333	1812	327	383	1130	1137
0.0150	256	2437	246	274	1811	1781
expt						1371[b]
						720[c]
ClH:ND$_3$						
0.0000	179	2275	179	191	1904	1561
0.0010	175	2188	183	202	1739	1416
0.0025	208	2055	188	232	1386	1212
0.0040	208	1783	197	288	971	1052
0.0055	419	504	239	355	1104	941
0.0100	318	1795	312	365	1135	1134
0.0150	244	2420	234	262	1801	1773
expt						1351[b]
						728[c]
ClD:NH$_3$						
0.0000	188	1638	187	192	1474	1266
0.0010	183	1577	191	197	1384	1139
0.0025	217	1482	196	209	1197	940
0.0040	216	1292	206	249	882	767
0.0055	459	347	457	337	743	663
0.0100	324	1326	319	358	840	892
0.0150	250	1777	240	258	1480	1431
ClD:ND$_3$						
0.0000	178	1638	177	182	1473	1263
0.0010	173	1577	181	186	1382	1136
0.0025	206	1482	186	199	1194	932
0.0040	205	1291	194	238	875	758
0.0055	438	344	431	323	719	654
0.0100	310	1311	306	343	837	886
0.0150	239	1760	230	247	1463	1419
expt						1113[b]
						550[c]

[a] Data taken from ref 4, except harmonic and one-dimensional anharmonic frequencies at 0.0055 au. See text. [b] Frequency in Ar from ref 37. [c] Frequency in N$_2$ from ref 37.

potential surface progressively moves away from the region of the traditional Cl−H···N hydrogen bond toward the proton-shared Cl···H···N region of the surface. The Cl−H distance increases with increasing field strength, while the Cl−N distance initially decreases to a minimum at a field of 0.0055 au. At this field the minimum on the potential surface is very broad, and the structure of the complex appears to be close to one with a quasi-symmetric proton-shared hydrogen bond. It is at this field strength that the proton-stretching frequency also exhibits its minimum computed value. We expect the lowest possible value for the proton-stretching frequency to occur at a field near 0.0055 au, which would produce the exact quasi-symmetric structure. Further increasing the field strength results in an increasing Cl−N distance in structures which assume greater ion-pair character. At sufficiently high fields the complex may be described as a hydrogen-bonded ion pair, and the proton-stretching motion becomes a perturbed N−H stretch.

It is apparent from Table 2 that there is little change in the expectation values of the Cl−H or Cl-D and Cl−N distances on deuteration of ammonia, as seen by comparing ClH:NH$_3$ with ClH:ND$_3$ and ClD:NH$_3$ with ClD:ND$_3$. At a field strength of 0.0055 au, however, the Cl−N distance is slightly greater in ClH:ND$_3$ than in ClH:NH$_3$. Replacement of HCl by DCl leads to slightly larger expectation values of the Cl−N distance at all fields except 0.0055 and 0.0100 au. Comparing ClH:NH$_3$ with ClD:NH$_3$ and ClH:ND$_3$ with ClD:ND$_3$ shows that the expectation value of the Cl−D distance is less than the expectation value of the Cl−H distance at weaker fields but greater at the higher fields of 0.0100 and 0.0150 au. In all of the isotopomers, the Cl−N distance decreases with increasing field strength, exhibits a minimum at a field of 0.0055 au, and then increases as the field strength increases. The expectation values of Cl−H and Cl−D distances increase with increasing field.

Table 3 reports harmonic proton and dimer frequencies obtained from the pseudotriatomic (reduced-dimensional) surfaces and one- and two-dimensional anharmonic proton- and dimer-stretching frequencies. Full-dimensional zero-field harmonic frequencies were reported in ref 4 for ClH:NH$_3$, and these were found to be similar to the reduced dimensional results. Therefore, full-dimensional frequencies are not reported for the deuterated complexes.

The differences between harmonic frequencies and one-dimensional anharmonic frequencies provide a crude estimate of the anharmonicity of the vibration. Except for the dimer frequencies in ClH:NH$_3$ and ClH:ND$_3$ at a field of 0.0055 au, the harmonic frequencies are similar to the one-dimensional anharmonic frequencies. That is, except for these two cases, anharmonicity is not significant for the dimer stretch in any of the isotopomers. In contrast, the proton-stretching motion is strongly anharmonic at all field strengths for all isotopomers, although it is greater for complexes with HCl than DCl. The harmonic frequencies are always significantly larger than the one-dimensional anharmonic frequencies, except at a field of 0.0055 au. At this field, the potential surface surrounding the minimum is broad and flat, and the harmonic proton-stretching frequencies are significantly lower than the one-dimensional anharmonic frequencies. Moreover, the computed harmonic proton-stretching frequencies for ClD:NH$_3$ and ClD:ND$_3$ at 0.0055 au are even lower than the computed dimer frequencies.

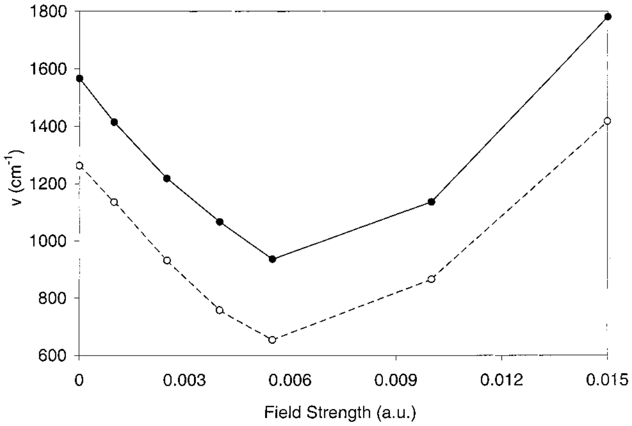

Figure 1. Proton-stretching frequencies for ClH:NH$_3$ and ClD:ND$_3$ as a function of field strength: ClH:NH$_3$, —; ClD:ND$_3$, ---.

It should also be noted that because of the flatness of the surface at 0.0055 au, harmonic and one-dimensional anharmonic frequencies are very sensitive to the minimum on the surface and the nature of the normal mode displacement vectors. The frequencies reported in Table 3 have been calculated using tighter convergence criteria for the minimum-energy configuration than was used in ref 4. As a result, these frequencies differ slightly from those previously reported.

The difference between the one- and two-dimensional dimer- and proton-stretching frequencies is an indication of the importance of coupling between these two modes. Coupling has a relatively small effect on the dimer stretching frequencies in all isotopomers at all field strengths except 0.0055 au. At this field coupling between the dimer- and proton-stretching modes increases the one-dimensional dimer stretching frequency of ClH:ND$_3$ by 116 cm^{-1}, while coupling decreases the one-dimensional dimer stretching frequencies of ClH:ND$_3$ and ClD:ND$_3$ by 120 and 108 cm^{-1}, respectively. In contrast, coupling between the dimer- and proton-stretching modes is much more important in determining proton-stretching frequencies, particularly at the weaker fields up to and including 0.0055 au. That is, it appears that coupling between dimer- and proton-stretching modes is important in complexes with traditional or proton-shared hydrogen bonds but is less important as the hydrogen bond acquires ion-pair character. In isotopomers with Cl−H−N hydrogen bonds, the one-dimensional anharmonic proton-stretching frequency is greater than the two-dimensional frequency at fields of 0.0055 au and lower, except at 0.0040 au. At this field the one-dimensional anharmonic frequencies have their lowest values. The complexes at fields less than 0.0055 au are on the traditional side of quasi-symmetric. The one- and two-dimensional frequencies are similar at the higher fields of 0.0100 and 0.0150 au when the complexes are on the ion-pair side of quasi-symmetric. In contrast, in complexes with Cl−D−N hydrogen bonds, the one-dimensional proton-stretching frequency is greater than the two-dimensional frequency except at a field strength of 0.0100 au. In all isotopomers, the proton-stretching frequency decreases with increasing field strength, has its lowest value for the near quasi-symmetric hydrogen-bonded structure at a field of 0.0055 au, and then increases with increasing field strength as the hydrogen bond assumes greater ion-pair character. The anharmonic proton-stretching frequencies for ClH:NH$_3$ and ClD:ND$_3$ are plotted as a function of field strength in Figure 1.

As evident from Table 3 and Figure 1, the proton-stretching frequency is reduced when the hydrogen-bonded proton is deuterated. Harmonic analysis gives a value of 0.71 for the ratio $\nu(D)/\nu(H)$. A comparison of the two-dimensional proton-stretching frequencies of ClH:NH$_3$ with ClD:NH$_3$ and ClH:ND$_3$ with ClD:ND$_3$ shows that $\nu(D)/\nu(H)$ is greater than 0.71 at all field strengths except 0.0055 au. At this field the hydrogen bond is near quasi-symmetric, and $\nu(D)/\nu(H)$ are 0.71 and 0.70, respectively. This is surprising, given that a quasi-symmetric proton-shared hydrogen bond is considered to be the most anharmonic in other respects. For the dimer stretch, deuteration of HCl leads to a ratio $\nu(D)/\nu(H)$ which varies from about 0.83 to 0.95, while deuteration of NH$_3$ gives a nearly constant value of 0.95 at all field strengths.

It is possible to compare the computed two-dimensional anharmonic proton-stretching frequencies with experimental frequencies obtained in Ar and N$_2$ matrixes.[37] The experimental frequencies for ClH:NH$_3$, ClH:ND$_3$, and ClD:ND$_3$ are also reported in Table 3. The frequencies in Ar are 1371, 1351, and 1113 cm^{-1}, respectively. The ClH:NH$_3$ complex in an Ar matrix has four strong IR absoprtion bands at 1371, 1289, 1072, and 733 cm^{-1}. The computed results support the assignment made by Barnes[37] of the band at 1371 cm^{-1} to the proton-stretching mode, since, for each isotopomer, the experimental frequency lies consistently between the computed two-dimensional anharmonic proton-stretching frequencies at field strengths of 0.0010 and 0.0025 au. The experimental frequencies in N$_2$ lie 216 and 213 cm^{-1} below the lowest computed frequencies for the quasi-symmetric complexes ClH:NH$_3$ and ClH:ND$_3$ at a field of 0.0055 au and 104 cm^{-1} below the computed frequency for ClD:ND$_3$ at this same field strength. These data justify further extension of a previous observation that ClH:NH$_3$ and its isotopomers have hydrogen bonds that are on the traditional side of quasi-symmetric in Ar and close to quasi-symmetric in N$_2$.

BrH:NH$_3$, BrH:ND$_3$, BrD:NH$_3$, and BrD:ND$_3$. The equilibrium structure of BrH:NH$_3$ is also stabilized by a traditional hydrogen bond, with a Br−N distance (R_e) of 3.247 Å and a Br−H distance of 1.462 Å, slightly elongated from the monomer distance of 1.407 Å. This structure is consistent with the experimental structure reported by Legon,[36] who noted that proton transfer from Br to N does not occur in this complex. However, as noted in ref 4, the potential surface surrounding the global minimum is relatively flat and is connected by a shallow valley to a second local Born−Oppenheimer minimum with a proton-shared hydrogen bond. The ground-state vibrational wave function for this complex is centered in this valley, so that the complex samples both the traditional and proton-shared regions of the surface in the ground vibrational state. As a result, the anharmonicity correction for the proton-stretching vibration is very large.

Table 4 presents the computed Br−N and Br−H distances (R_e) and expectation values of these distances (R_o) for all isotopomers as a function of field strength. Deuteration of HBr or NH$_3$ has only a small effect on the expectation values of Br−N and Br−H or Br−D distances. In all isotopomers, the expectation value of the Br−N distance initially decreases with increasing field strength, reaches a minimum at a field strength of 0.0025 au, and then subsequently increases. As a function of increasing field strength the hydrogen bond type changes from traditional at low fields, to proton-shared at higher fields (close to quasi-symmetric at a field of 0.0025 au), and then to ion pair at the highest fields.

Table 5 reports harmonic and anharmonic frequencies for the dimer- and proton-stretching vibrations of BrH:NH$_3$ and its isotopomers. Once again, the harmonic frequencies for the dimer stretch are similar to the one-dimensional anharmonic frequen-

TABLE 4: Equilibrium (R_e) and Expectation Values (R_0) in the Ground Vibrational State for the Br−N (R) and Br−H (R_2) Distances (Å) in BrH:NH$_3$ and Its Deuterated Analogues

			BrH:NH$_3$[a]		BrH:ND$_3$		BrD:NH$_3$		BrD:ND$_3$	
field	R_e	R_{2e}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}
0.0000	3.247	1.462	3.053	1.623	3.051	1.625	3.075	1.588	3.072	1.591
0.0005	3.224	1.469	3.037	1.651	3.036	1.653	3.040	1.633	3.037	1.636
0.0010	2.976	1.778	3.027	1.676	3.025	1.677	3.018	1.672	3.018	1.674
0.0025	2.993	1.830	3.016	1.740	3.014	1.740	3.015	1.741	3.007	1.756
0.0040	3.009	1.868	3.021	1.794	3.021	1.794	3.015	1.812	3.015	1.813
0.0080	3.068	1.965	3.066	1.910	3.065	1.910	3.067	1.928	3.066	1.928
0.0120	3.152	2.075	3.142	2.027	3.142	2.027	3.147	2.044	3.147	2.044

[a] Data taken from ref 4.

TABLE 5: Harmonic and Anharmonic Proton and Dimer Stretching Frequencies (cm^{-1}) as a Function of Field Strength (au) for BrH:NH$_3$ and Its Deuterated Analogues

	harmonic: "triatomic" surface		anharmonic			
			dimer		proton	
field	dimer	proton	1-D	2-D	1-D	2-D
		BrH:NH$_3$[a]				
0.0000	133	1990	139	210	1469	908
0.0005	112	1883	141	252	1238	865
0.0010	376	1002	370	293	979	833
0.0025	351	1369	348	362	971	809
0.0040	342	1683	329	362	1054	954
0.0080	286	2180	277	305	1513	1544
0.0120	221	2259	214	240	2062	2041
expt						729[b] 1386[c]
		BrH:ND$_3$				
0.0000	125	1990	130	201	1466	896
0.0005	106	1882	132	241	1232	855
0.0010	354	997	349	279	991	828
0.0025	331	1372	328	340	986	798
0.0040	321	1674	310	340	1062	954
0.0080	269	2170	261	287	1509	1539
0.0120	207	2541	202	226	2053	2032
		BrD:NH$_3$				
0.0000	133	1421	138	142	1215	633
0.0005	112	1346	140	183	1128	570
0.0010	362	740	358	241	536	518
0.0025	340	1016	337	364	587	536
0.0040	332	1231	319	347	740	758
0.0080	278	1593	270	288	1244	1247
0.0120	215	1864	209	226	1624	1601
		BrD:ND$_3$				
0.0000	124	1420	129	135	1214	620
0.0005	105	1345	131	177	1125	559
0.0010	343	730	339	234	558	508
0.0025	322	1004	319	343	602	538
0.0040	314	1218	302	328	746	754
0.0080	263	1578	255	273	1232	1238
0.0120	203	1846	198	214	1608	1587

[a] Data taken from ref 4. [b] Frequency in Ar from ref 12. [c] Frequency in N$_2$ from ref 12.

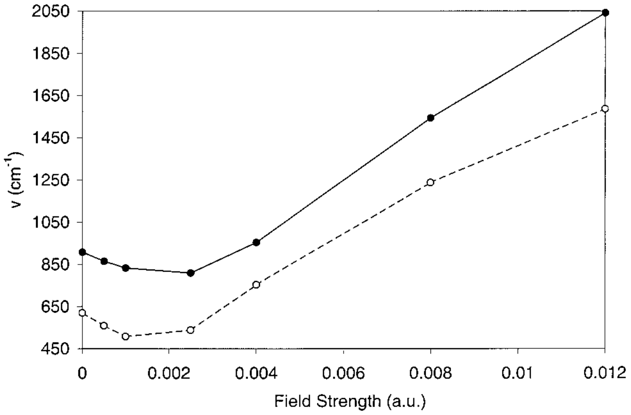

Figure 2. Proton-stretching frequencies for BrH:NH$_3$ and BrD:ND$_3$ as a function of field strength: BrH:NH$_3$, —; BrD:ND$_3$, ---.

cies, but the harmonic frequencies for the proton stretch are usually significantly higher than the one-dimensional anharmonic frequencies. This means that, in all isotopomers, anharmonicity is not significant for the dimer stretch, but it is significant for the proton stretch. Coupling between the dimer- and proton-stretching modes is very important at lower fields but becomes less important at higher fields as these complexes assume greater ion-pair character. As evident from Table 5, increasing the strength of the electric field leads initially to relatively small decreases in the proton-stretching frequencies, much less than observed for ClH:NH$_3$. For BrH:NH$_3$ the proton-stretching frequency has its minimum value of 809 cm^{-1} at a field of 0.0025 au. This value is only 100 cm^{-1} lower than the computed gas-phase value at zero field and 80 cm^{-1} higher than the experimental Ar matrix value. Thus, both structural and frequency data suggest that BrH:NH$_3$ at a field strength of 0.0025 au or in an Ar matrix most closely corresponds to a quasi-symmetric hydrogen-bonded complex. In an N$_2$ matrix the experimental proton-stretching frequency is 1386 cm^{-1}. The computed frequencies at field strengths of 0.0040, 0.0080, and 0.0120 au are 954, 1544, and 2041 cm^{-1}, respectively. These data suggest that in an N$_2$ matrix the BrH:NH$_3$ complex approaches a hydrogen-bonded ion pair.

Deuteration of NH$_3$ has only a minor effect on the proton-stretching frequencies of BrH:ND$_3$, and its structure and IR spectrum in Ar and N$_2$ are similar to those of BrH:NH$_3$. In contrast, replacement of HBr by DBr does have a major isotopic effect, as expected. For both BrD:NH$_3$ and BrD:ND$_3$ increasing the strength of the external electric field initially decreases proton-stretching frequencies, which have their minimum values at a field of 0.0010 au. At this field these frequencies are only 115 and 112 cm^{-1}, respectively, lower than the zero-field gas-phase values. This suggests that the complexes with DBr become quasi-symmetric at a slightly lower field than those with HBr. The ratio $\nu(D)/\nu(H)$ for BrH:NH$_3$ and BrD:NH$_3$ and for BrH:ND$_3$ and BrD:ND$_3$ are slightly lower than the harmonic value of 0.71 at zero field, decrease to a minimum value of 0.62 and 0.61 at a field of 0.0010 au, and then subsequently increase to their largest values of 0.81 and 0.80, respectively, at a field of 0.0080 au. The proton-stretching frequencies of BrH:NH$_3$ and BrD:ND$_3$ are plotted as a function of field strength in Figure 2. Unfortunately, there are no experimental data available for the deuterated complexes.

ClH:N(CH$_3$)$_3$ and BrH:N(CH$_3$)$_3$ and Their Deuterated Analogues. Because trimethylamine is a significantly stronger base than ammonia, the equilibrium structures of ClH:N(CH$_3$)$_3$ and BrH:N(CH$_3$)$_3$ are no longer stabilized by traditional X−H···N hydrogen bonds. The zero-field equilibrium structure

TABLE 6: Equilibrium (R_e) and Expectation Values (R_0) in the Ground Vibrational state for the X−N (R) and X−H (R_2) Distances (Å) in $ClH:N(CH_3)_3$ and $BrH:N(CH_3)_3$ and Their Deuterated Analogues

			$ClH:N(CH_3)_3$[a]		$ClH:N(CD_3)_3$		$ClD:N(CH_3)_3$		$ClD:N(CD_3)_3$	
field	R_e	R_{2e}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}
0.0000	2.825	1.658	2.850	1.615	2.850	1.615	2.843	1.624	2.843	1.624
0.0010	2.836	1.685	2.855	1.640	2.854	1.640	2.849	1.651	2.849	1.651
0.0040	2.872	1.752	2.880	1.706	2.880	1.706	2.877	1.719	2.877	1.719
			$BrH:N(CH_3)_3$[a]		$BrH:N(CD_3)_3$		$BrD:N(CH_3)_3$		$BrD:N(CD_3)_3$	
field	R_e	R_{2e}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}	R_0	R_{20}
0.0000	2.983	1.870	2.991	1.830	2.991	1.830	2.989	1.842	2.989	1.842
0.0010	2.993	1.887	3.001	1.849	3.001	1.849	2.999	1.861	2.999	1.861
0.0040	3.027	1.937	3.032	1.904	3.032	1.904	3.031	1.915	3.031	1.914

[a] Data taken from ref 4.

of $ClH:N(CH_3)_3$ has a proton-shared hydrogen bond, while the structure of $BrH:N(CH_3)_3$ approaches that of a hydrogen-bonded ion pair, in agreement with Legon's characterization of these complexes.[36] In our previous work[4] it was observed that even a small external electric field applied along the hydrogen bonding direction increases the ion-pair character of the hydrogen bond in these complexes. Because these complexes behave similarly with respect to external electric fields, we will treat them together in this section.

Expectation values of the X−H and X−N distances in the complexes $ClH:N(CH_3)_3$ and $BrH:N(CH_3)_3$ and their deuterated analogues are reported in Table 6. Deuteration of timethylamine has essentially no effect on the expectation values of X−N and X−H distances. Deuteration of HCl or HBr leads to small decreases in the expectation values of Cl−N and Br−N distances and small increases in Cl−D and Br−D distances relative to Cl−H and Br−H, respectively. For all isotopomers, expectation values of Cl−N and Br−N distances and of Cl−H, Cl-D, Br−H, and Br-D distances increase with increasing field strength.

Harmonic and anharmonic dimer- and proton-stretching frequencies for $ClH:N(CH_3)_3$ and its isotopomers are reported in Table 7. Harmonic and anharmonic dimer-stretching frequencies decrease with increasing field strength and, at a given field strength, have similar values in all of the isotopomers. In each complex the one- and two-dimensional anharmonic frequencies bracket the harmonic dimer frequency. The anharmonic correction for the dimer stretching mode is obviously quite small.

The proton-stretching frequencies increase with increasing field strength in $ClH:N(CH_3)_3$ and its isotopomers as these complexes assume greater ion-pair character, and the proton-stretching mode becomes a perturbed N−H stretch. The absolute difference between the harmonic and two-dimensional anharmonic proton-stretching frequencies is larger in the complexes with HCl than DCl, and in each isotopomer these frequencies increase with increasing field strength. Deuteration of trimethylamine has no effect on proton-stretching frequencies, while deuteration of HCl lowers both harmonic and anharmonic proton-stretching frequencies, as expected. The ratio $\nu(D)/\nu(H)$ for $ClH:N(CH_3)_3$ and $ClD:N(CH_3)_3$ and for $ClH:N(CD_3)_3$ and $ClD:N(CD_3)_3$ is close to the harmonic ratio at zero field (0.72 and 0.71, respectively) and increases to 0.76 at a field of 0.0040 au. The experimental proton-stretching frequency of $ClH:N(CH_3)_3$ in Ar is 1486 cm^{-1}, in good agreement with the value of 1478 cm^{-1} computed at a field strength of 0.0040 au. It is anticipated that, at a slightly greater field strength, the computed proton-stretching frequency would increase to the N_2 matrix value of 1615 cm^{-1}. This is consistent with the greater ion-pair character of this complex in N_2 compared to Ar. Experimental proton-stretching frequencies for $ClD:N(CH_3)_3$ have also been reported.[13] In Ar, the experimental value is 1244 cm^{-1}. This value is also higher than the computed proton-stretching frequency of 1118 cm^{-1} at a field strength of 0.0040 au. On the basis of this and previous studies, it is anticipated that increasing the field strength would lead to a further increase in the proton-stretching frequency to give the experimental frequency of 1344 cm^{-1} for $ClD:N(CH_3)_3$ in an N_2 matrix.

TABLE 7: Harmonic and Anharmonic Proton and Dimer Stretching Frequencies (cm^{-1}) as a Function of Field Strength (au) for $ClH:N(CH_3)_3$ and Its Deuterated Analogues

	harmonic: "triatomic" surface		anharmonic			
			dimer		proton	
field	dimer	proton	1-D	2-D	1-D	2-D
		$ClH:N(CH_3)_3$[a]				
0.0000	314	1406	310	320	1344	1134
0.0010	303	1579	298	316	1370	1221
0.0040	272	1938	266	289	1499	1478
expt						1486[b] 1615[c]
		$ClH:N(CD_3)_3$				
0.0000	306	1405	303	313	1345	1134
0.0010	296	1579	290	308	1372	1223
0.0040	265	1933	260	282	1498	1476
		$ClD:N(CH_3)_3$				
0.0000	312	1004	309	322	898	811
0.0010	302	1129	296	313	941	896
0.0040	271	1382	265	282	1104	1118
expt						1244[b] 1344[c]
		$ClD:N(CD_3)_3$				
0.0000	305	1002	302	314	900	810
0.0010	295	1126	289	306	942	893
0.0040	265	1378	259	275	1103	1116

[a] Data taken from ref 4. [b] Frequency in Ar from ref 13. [c] Frequency in N_2 from ref 13.

Table 8 reports dimer- and proton-stretching frequencies for $BrH:N(CH_3)_3$ and its isotopomers. Deuteration of either HBr or $N(CH_3)_3$ has little effect on dimer-stretching frequencies. Both harmonic and anharmonic one- and two-dimensional dimer frequencies for each isotopomer are very similar at a given field strength and decrease with increasing field. Deuteration of $N(CH_3)_3$ has no effect on proton-stretching frequencies, but deuteration of HBr reduces these frequencies. The ratios $\nu(D)/\nu(H)$ for $BrH:N(CH_3)_3$ and $BrD:N(CH_3)_3$ and for $BrH:N(CD_3)_3$ and $BrD:N(CD_3)_3$ are 0.75 or 0.76, always higher than the harmonic value of 0.71. The experimental proton-stretching frequency of $BrH:N(CH_3)_3$ in Ar is 1660 cm^{-1},[12] a value close to the computed value of 1683 cm^{-1} at a field of 0.0010 au. The experimental proton-stretching vibration in N_2 has been assigned to a doublet at 1890 and 1872 cm^{-1}.[12] These values are slightly lower than the computed value of 1933 cm^{-1} at a

TABLE 8: Harmonic and Anharmonic Proton and Dimer Stretching Frequencies (cm^{-1}) as a Function of Field Strength (au) for $BrH:N(CH_3)_3$ and Its Deuterated Analogues

	harmonic: "triatomic" surface		anharmonic			
			dimer		proton	
field	dimer	proton	1-D	2-D	1-D	2-D
			$BrH:N(CH_3)_3$[a]			
0.0000	232	2004	230	239	1622	1595
0.0010	226	2102	224	233	1697	1683
0.0040	209	2326	205	214	1926	1933
expt						1660[b] 1890, 1872[c]
			$BrH:N(CD_3)_3$			
0.0000	224	2002	221	230	1622	1593
0.0010	218	2097	215	224	1696	1682
0.0040	201	2324	197	206	1925	1931
			$BrD:N(CH_3)_3$			
0.0000	232	1429	228	235	1207	1207
0.0010	225	1497	223	229	1270	1274
0.0040	208	1660	204	210	1448	1455
			$BrD:N(CD_3)_3$			
0.0000	223	1427	220	226	1205	1206
0.0010	217	1495	214	221	1268	1272
0.0040	200	1656	196	148	1445	1450

[a] Data taken from ref 4. [b] Frequency in Ar from ref 12. [c] Frequency in N_2 from ref 12.

field strength of 0.0040 au. To our knowledge, no experimental data have been reported for the deuterated complexes.

Conclusions

An ab initio study of the hydrogen-bonded complexes of the deuterated analogues of $ClH:NH_3$, $BrH:NH_3$, $ClH:N(CH_3)_3$, and $BrH:N(CH_3)_3$ has been carried out. The results of this investigation support the following conclusions: (1) There is little change in the expectation values of Cl−N, Br−N, Cl−H, or Br−H distances upon deuteration. The field dependence of these distances is also unchanged by deuteration. (2) Deuteration has little effect on dimer-stretching frequencies. Deuteration of NH_3 or $N(CH_3)_3$ has little effect on proton-stretching frequencies, but deuteration of HCl or HBr significantly reduces proton-stretching frequencies, as expected. The ratio $\nu(D)/\nu(H)$ in corresponding pairs of isotopomers may be less than, equal to, or greater than the harmonic ratio of 0.71. (3) The proton-stretching frequencies for the complexes $ClH:NH_3$, $ClH:ND_3$, $ClD:NH_3$, and $ClD:ND_3$ initially decrease with increasing field strength, exhibit minimum values at a field of 0.0055 au, and then increase as the field strength further increases The computed frequencies for $ClH:NH_3$, $ClH:ND_3$, and $ClD:ND_3$ at field strengths of 0.0010 and 0.0025 au bracket the experimental frequencies measured in Ar matrices, while the computed frequencies at a field strength of 0.0055 au lie 100−200 cm^{-1} above the experimental frequencies in N_2. The computed results suggest that these complexes are stabilized by traditional hydrogen bonds in Ar and by hydrogen bonds which are close to quasi-symmetric in N_2. The computed anharmonic proton-stretching frequencies also support the assignment of the band at 1371 cm^{-1} in the Ar matrix spectrum of $ClH:NH_3$ to the proton-stretching vibration. (4) The proton-stretching frequencies of $BrH:NH_3$ and its isotopomers initially decrease with increasing field strength. Complexes with HBr exhibit minimum values at a field of 0.0025 au, while complexes with DBr exhibit minimum values at a field of 0.0010 au, although the frequencies at fields of 0.0010 and 0.0025 differ by only 18 and 30 cm^{-1}, respectively. It appears that these complexes have proton-shared, nearly quasi-symmetric hydrogen bonds in Ar and hydrogen bonds with considerable ion-pair character in N_2. (5) The proton-stretching frequencies of $ClH:N(CH_3)_3$ and $BrH:N(CH_3)_3$ and their isotopomers increasing with increasing field strength. The experimental proton-stretching frequencies of $ClH:N(CH_3)_3$ and $ClD:N(CH_3)_3$ are similar to the computed frequencies at a field of 0.0040 au. The experimental proton-stretching frequency of $BrH:N(CH_3)_3$ in Ar lies between the computed frequencies at fields of 0.0000 and 0.0010 au, while the experimental frequencies in N_2 lie between the computed values at fields of 0.0010 and 0.0040 au. These data suggest that all of these complexes have ion-pair character in inert matrices, with the ionicity of $BrH:N(CH_3)_3$ being greater than $ClH:N(CH_3)_3$. (6) The agreement between the computed proton-stretching frequencies and experimental frequencies in Ar and N_2 matrices for the normal and deuterated complexes of HCl and HBr with ammonia and trimethylamine (a) emphasizes the anharmonic nature of the proton-stretching vibration and the importance of coupling between the dimer- and proton-stretching modes and (b) supports the validity of modeling matrix effects on the structures and vibrational spectra of hydrogen-bonded complexes by applying external electric fields.

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