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Vibrational Spectroscopic and NMR Properties of Hydrogen-Bonded Complexes: Do They Tell Us the Same Thing?

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Abstract: Both vibrational infrared and NMR spectroscopy are probes of the hydrogen bond. The ab initio calculations reported in this paper demonstrate that relationships exist among the X−Y distance in an X−H−Y hydrogen bond, the anharmonic proton-stretching frequency, the ^{1}H NMR chemical shift, and the X−Y spin−spin coupling constant. Structural information related to the type of hydrogen bond present may be inferred from these data.

Introduction

Infrared spectroscopy has traditionally been the spectroscopic tool most frequently used to investigate the hydrogen bond.[1] More recently, NMR has become a second spectroscopic probe of hydrogen bonding, particularly in biochemical systems.[2] Both provide diagnostic signatures for the formation of a hydrogen bond. The infrared spectrum of a hydrogen-bonded complex with an X−H···Y bond typically shows a very intense band due to the proton-stretching motion, which is shifted to lower frequency relative to the X−H band in the corresponding monomer. There are a number of NMR observables that also provide indirect evidence for the formation of a hydrogen bond, perhaps the most characteristic being a large downfield chemical shift of the hydrogen-bonded proton relative to the monomer. Recent experimental[3−7] and theoretical[8] work has shown that heavy atom coupling constants across the hydrogen bond ($^2J_{\mathrm{XY}}$) are also diagnostic of hydrogen bond formation. The “type” of hydrogen bond formed, however, is also an important factor in determining the spectroscopic properties of hydrogen-bonded complexes.[8−10] It has been postulated that particularly short, strong hydrogen bonds may play an important role in many enzyme-catalyzed reactions.[11] In this paper we relate the vibrational and NMR spectroscopic properties of hydrogen-bonded complexes, and show that these properties are correlated with and dependent upon the structural type of the hydrogen bond.

Hydrogen bonds may be classified as traditional, proton-shared, or ion-pair. A traditional X−H···Y hydrogen bond has a normal (as opposed to short) intermolecular X−Y distance, an X−H distance slightly elongated relative to the X−H distance in the monomer, and a Y−H distance that is much longer than a covalent Y−H distance. Ion-pair $\mathrm{Y{-}H^+{\cdots}X^-}$ hydrogen bonds are formed after proton transfer from X to Y. These have X−Y distances that are comparable to X−Y distances in traditional hydrogen bonds, long X−H distances, and Y−H distances slightly elongated relative to the Y−H distance in the corresponding cation. Intermediate between these two is the proton-shared X···H···Y hydrogen bond. This type is characterized by a short X−Y distance, and X−H and Y−H distances that are longer than the X−H distance in a traditional hydrogen bond, and the Y−H distance in a hydrogen-bonded ion-pair. We define a quasisymmetric hydrogen bond as a special type of proton-shared hydrogen bond in which the proton is shared equally by X and Y, that is, the forces on H from X and Y are equal.[10,12] Our definition makes no a priori assumption about the relative X−H and Y−H distances in the quasisymmetric structure. Other workers have characterized hydrogen bond type in such systems in terms of the coordinate $q = {}^1/_2(r_1 - r_2)$, where r_1 is the X−H distance and r_2 the Y−H distance.[13] This coordinate is effectively a symmetry coordinate and is only strictly valid for the case of a symmetric hydrogen-bonded complex.

Having defined hydrogen bond structure type, we now focus on the relationships between spectroscopic properties and the structure of the hydrogen-bonded complex. In a recent paper the computed ^{1}H NMR chemical shifts in hydrogen-bonded complexes were reported.[9] A linear relationship was observed between increasing proton chemical shift relative to the corresponding neutral monomer and increasing binding energy within two series of complexes. The first series included complexes

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with Cl−H−N and Cl−H−Cl hydrogen bonds, while the second included complexes with N−H−N, N−H−O, and O−H−O hydrogen bonds. Although the linear relationship between binding energy and proton chemical shift does not hold across the two series, complexes stabilized by proton-shared hydrogen bonds were found to have similar chemical shifts of about 20 ppm for the hydrogen-bonded proton, independent of binding energy.

A subsequent paper[8] reported the computed X−Y spin−spin coupling constants across the X−H−Y hydrogen bond (X, Y = N, O), and found that the total coupling constant ($^{2}J_{XY}$) is dominated by the Fermi-contact term. Both the Fermi-contact term and the total coupling constant are distance dependent, increasing with decreasing X−Y distance. Since complexes with proton-shared X···H···Y hydrogen bonds have short intermolecular distances and low electron densities on the hydrogen-bonded proton, these complexes have larger X−Y spin−spin coupling constants relative to complexes stablized by traditional X−H···Y hydrogen bonds.[8]

The equilibrium structures and proton-stretching frequencies of four hydrogen-bonded complexes formed between hydrogen halides (HCl and HBr) and ammonia (NH_3) and trimethylamine [$N(CH_3)_3$] have been recently investigated as a function of the strength of external electric fields imposed along the hydrogen-bonding X−H−N direction.[10] Because of the anharmonicity inherent in the potential energy surfaces of these complexes, an anharmonic two-dimensional treatment of vibration was employed. The changes that occurred in X−N distances and anharmonic proton-stretching frequencies as a function of field strength were shown to be dependent on the strength of the field, and the nature of the equilibrium structure of the complex at zero field. It was observed that equilibrium X−N distances are short and proton-stretching frequencies low in complexes with proton-shared hydrogen bonds. The shortest distances and lowest frequencies are found in complexes in which the hydrogen bond is quasisymmetric. This work also provided insight into the apparently disparate matrix effects observed for these complexes in Ar and N_2 matrices.[10]

The ClH:NH_3 complex studied in ref 10 provides a protopytical example of a hydrogen bond. Since the structure of ClH:NH_3 changes from traditional to proton-shared to hydrogen-bonded ion-pair as the field strength increases,[10] it is possible to examine the changes in spectroscopic properties that accompany these structural changes using a single reference system. Both ^{35}Cl and ^{37}Cl, however, have non-zero quadrupole moments, making coupling constants involving these atoms not experimentally observable. Nevertheless, the ClH:NH_3 complex is an appealing theoretical model. It is our expectation that the trends observed for this complex will be valid in a wide range of hydrogen-bonded systems.

In this paper, we report the structures, proton-stretching frequencies, ^{1}H NMR chemical shifts, and ^{35}Cl−^{15}N spin−spin coupling constants computed for the ClH:NH_3 complex as explicit functions (geometry and frequency) and implicit functions (chemical shift and coupling constant) of the strength of the applied external field. To our knowledge, this is the first attempt to relate these properties using the results of high-level ab initio calculations.

Methods

To examine the structures and proton-stretching frequencies of ClH:NH_3 as a function of field strength, two-dimensional potential surfaces in the Cl−H and N−H distances were generated from sets of ab initio data points computed at second-order Møller−Plesset perturbation theory [MBPT(2) = MP2][14−17] by using Dunning's correlation-consistent valence double-split basis set augmented with diffuse functions on Cl and N (aug'-cc-pVDZ).[18−20] A model two-dimensional nuclear Schrödinger equation was solved to obtain anharmonic wave functions and dimer- and proton-stretching frequencies on each surface. Details are reported in ref 10. Proton chemical shifts and heavy-atom spin−spin coupling constants were not computed in a field, but rather the geometries used were those corresponding to the equilibrium Cl−H and N−H distances obtained from the two-dimensional surfaces at various field strengths. Thus, we assume that the NMR properties are dominated by structural changes, and that any additional polarization effects on the wave function are relatively minor.

The proton chemical shifts were computed at MP2 using the gauge-invariant atomic orbital (GIAO) method,[21] and spin−spin coupling constants were obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations using the configuration interaction (CI-like) approximation,[22] a level of theory that gives quantitatively accurate coupling constants when compared with experimentally measured values.[8,22−25] All NMR properties were evaluated using Alhrich's (qzp, qz2p) basis set.[26] The ab initio data points needed to construct the surfaces were obtained using Gaussian 98,[27] while the NMR properties were computed using ACESII.[28] These calculations were performed on the Cray T94 and SGI-Origin computers at the Ohio Supercomputer Center, and on the computing facilities at the University of Sydney.

Results and Discussion

Table 1 presents the equilibrium Cl−N distance (R_e) obtained from the two-dimensional surfaces and the anharmonic two-dimensional proton-stretching frequency obtained at each field strength. Table 1 also includes the ^{1}H NMR chemical shift of the hydrogen-bonded proton relative to HCl, and the ^{35}Cl−^{15}N spin−spin coupling constant, $^{2}J_{ClN}$, at the minimum energy geometry calculated at each field strength. These data are shown graphically in Figure 1, and the obvious correlations evident from this figure will be discussed below. The equilibrium Cl−N distances and the proton-stretching frequencies reported in Table 1 are taken from ref 10.

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Table 1. Equilibrium Cl−N Distances (R_e, Å), Two-Dimensional Proton-Stretching Frequencies (υ_{proton}, cm^{-1}), Proton Chemical Shifts ($\delta[\delta$(ppm)]), and Spin−Spin coupling constants ($^2J_{ClN}$, Hz) for ClH:NH$_3$ as Explicit and Implicit Functions of External Field Strength (au)

field	R_e(Cl−N)	υ_{proton}	$\delta[\delta$(ppm)][a]	$^2J_{ClN}$[b]
0.0000	3.080	1567	10.0	5.7
0.0010	3.056	1415	10.8	6.1
0.0025	3.019	1219	12.0	6.9
0.0040	2.975	1067	13.6	8.0
0.0055	2.832	936	20.9	11.8
0.0100	2.896	1137	19.1	9.1
0.0150	3.004	1781	16.4	6.7

[a] The chemical shift is given relative to the proton chemical shift for HCl. [b] Absolute value of $^2J_{ClN}$; all coupling constants predicted here are negative.

Table 2. Paramagnetic Spin−Orbit (PSO), Diamagnetic Spin−Orbit (DSO), Fermi-Contact (FC), and Spin-Dipole (SD) Contributions to the Total Spin−Spin Coupling Constant ($^2J_{ClN}$) for ClH:NH$_3$ as Implicit Functions of Field Strength[a]

field	PSO	DSO	FC	SD	$^2J_{ClN}$
0.0000	0.4	0.0	−5.9	−0.2	−5.7
0.0010	0.4	0.0	−6.3	−0.2	−6.1
0.0025	0.5	0.0	−7.1	−0.3	−6.9
0.0040	0.5	0.0	−8.2	−0.3	−8.0
0.0055	0.7	0.0	−12.2	−0.3	−11.8
0.0100	0.6	0.0	−9.5	−0.2	−9.1
0.0150	0.5	0.0	−7.0	−0.2	−6.7

[a] $^2J_{ClN}$ and components of $^2J_{ClN}$ in Hz; field strength in au.

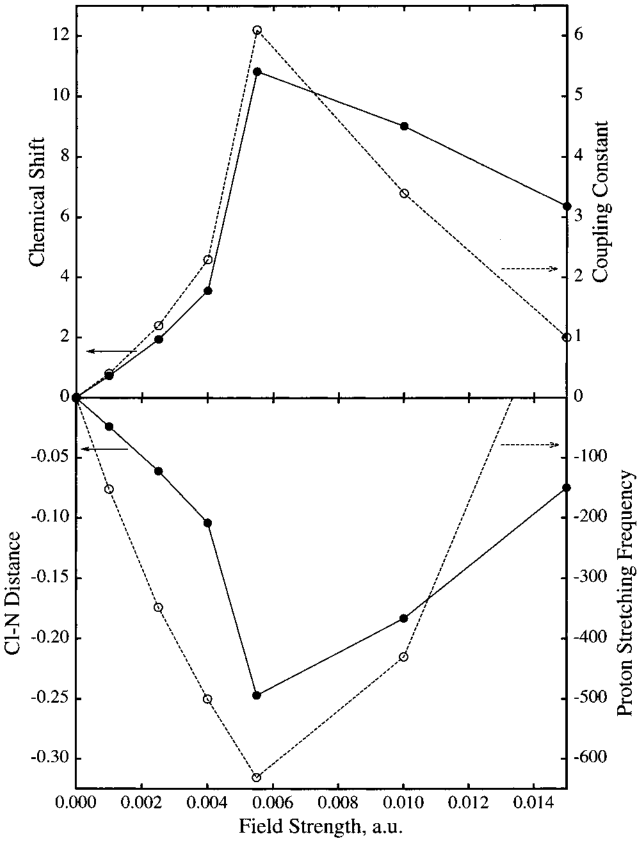

Figure 1. Vibrational and NMR properties of the ClH:NH$_3$ complex as a function of the strength of an external electric field imposed along the Cl−H−N direction. These plots have been made relative to a value of 0.0 for the property at zero field. The absolute values of the properties are given in Table 1. The upper plot shows the proton chemical shift (solid line) and the Cl−N spin−spin coupling constant (dashed line) as implicit functions of field strength. The lower plot shows the proton-stretching frequency (dashed line) and the equilibrium Cl−N distance (solid line) as explicit functions of field strength.

It was observed in ref 10 that the effect of applying electric fields of progressively increasing strengths on the ClH:NH$_3$ complex is to change the structure and therefore the hydrogen bond type from a traditional Cl−H•••N hydrogen bond at zero field, to a proton-shared Cl•••H•••N hydrogen bond at intermediate fields, to an ion-pair N−H$^+$•••Cl$^-$ hydrogen bond at higher fields. The structural changes are evident from the decrease in the equilibrium Cl−N distance, which has its minimum value at a field strength of 0.0055 au. At this field strength, the Cl•••H•••N hydrogen bond is essentially quasisymmetric. Further increasing the strength of the external field leads to an increase in the Cl−N distance as the complex assumes greater ion-pair character. The proton-stretching frequencies reflect these structural changes. At zero field the proton stretch is a perturbed Cl−H stretch. As the field increases, the proton-stretching frequency decreases to its minimum value for the quasisymmetric hydrogen-bonded structure at a field strength of 0.0055 au. Further increasing the external field pushes the proton closer to the nitrogen as the complex assumes increasing ion-pair character. At fields of 0.0100 and 0.0150 au, the proton-stretching frequency is better described as a perturbed N−H stretching vibration. The correlation between the Cl−N distance and the proton-stretching frequency is apparent from Figure 1.

Figure 1 also shows that two NMR properties, the ^{1}H NMR chemical shift of the hydrogen-bonded proton relative to HCl and the ^{35}Cl−^{15}N spin−spin coupling constant, vary implicitly with field strength in a way analogous to the variations observed in Cl−N distances and proton-stretching frequencies. The proton chemical shift increases as the equilibrium geometry changes in response to increasing field strength, attaining a maximum value of 20.9 ppm for the complex stabilized by a quasisymmetric hydrogen bond at a field of 0.0055 au. This result is in agreement with ref 9, which also found that ^{1}H NMR chemical shifts in proton-shared hydrogen bonds have a maximum value of about 20 ppm relative to the monomer. In this type of hydrogen bond the proton is deshielded, that is, the electron density at the proton is decreased relative to traditional and ion-pair hydrogen bonds. Table 2 shows that the ^{35}Cl−^{15}N spin−spin coupling constant across the Cl−H−N hydrogen bond is dominated by the Fermi-contact term, also in agreement with ref 8. Again, the absolute value of the coupling constant for the hydrogen-bonded Cl and N atoms increases as the equilibrium geometry changes in response to increasing field strength, attains its maximum value in the structure with a quasisymmetric hydrogen bond at a field of 0.0055 au, and then subsequently decreases at higher field strengths. Since the Fermi-contact term has been shown to be distance-dependent,[8] the coupling between Cl and N is most effective when the Cl−N distance is shortest, as it is in the quasisymmetric hydrogen-bonded structure. Similar relationships among F−F distance, proton chemical shift, and $^2J_{FF}$ have also been observed experimentally in small fluorine-containing clusters,[4] and the coupling constants have been reproduced by EOM-CCSD calculations.[25]

It should be noted that the NMR properties presented in this work have been calculated in the absence of a field, but at geometries determined from multidimensional surface calculations in the presence of electric fields imposed along the hydrogen-bonding direction.[10] In this way, field effects have been included implicitly in the NMR calculations. How would the presence of a field change the computed NMR properties? Over and above any change in geometry, the applied field will polarize the wave function and shift electron density from the

N and the ammonia hydrogens, through the hydrogen bond toward Cl. This will increase the electron density on the hydrogen-bonded proton, and may be expected to decrease the relative chemical shift by increasing proton shielding, and also reduce $^2J_{\mathrm{ClN}}$. These effects will become larger as the field increases. We expect, however, that because the distances involved are large, the effects will be relatively minor when compared to gross changes in equilibrium geometry. Explicit investigations of field effects on NMR properties will be the subject of future work.

The relationships evident from Figure 1 are dramatic. As the structure of the hydrogen-bonded complex changes, so do the proton-stretching frequencies, the hydrogen-bonded proton chemical shift, and the heavy-atom spin−spin coupling constant across the hydrogen bond. These changes are intimately related. It should be noted that an even better correlation of vibrational frequency with intermolecular Cl−N distance is observed when the expectation value of the Cl−N distance (R_0) in the ground vibrational state is used instead of the equilibrium distance (R_e).[10] However, since R_0 values are much more difficult to calculate than R_e values and are generally not available, R_e has been used here as an indication of intermolecular distance. It is, in principle, possible to calculate shielding constants or coupling constants for particular ro-vibrational states by averaging these over the ro-vibrational wave function. Indeed, the difference between a shielding constant calculated at the equilibrium geometry and one averaged over nuclear motion may be significant.[29] Given that the ClH:NH$_3$ complex is known to behave anharmonically,[10] such corrections may be important, and may be envisaged to improve the correlation between the NMR properties, R_0, and the proton-stretching frequency.

Concluding Remarks

It has been demonstrated previously that the environment influences the vibrational spectroscopic properties of hydrogen-bonded complexes. The correlation between vibrational and NMR spectroscopic properties observed in this work demonstrates that the environment should also influence experimental NMR proton chemical shifts for hydrogen-bonded protons, and heavy-atom spin−spin coupling constants across hydrogen bonds. In turn, these properties provide information about the structure of the hydrogen-bonded complex in terms of the type of hydrogen bond present, and the intermolecular distance. As NMR is often the only method available to study hydrogen bonds in biochemical systems, an understanding of how hydrogen bond type influences observed spectroscopic properties will enable NMR to become a far more useful structural tool for studying hydrogen-bonded systems.

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