Article

On the Correlation between Bond-Length Change and Vibrational Frequency Shift in Hydrogen-Bonded Complexes: A Computational Study of Y···HCl Dimers (Y = N, CO, BF)

Sean A. C. McDowell, and A. David Buckingham

J. Am. Chem. Soc., **2005**, 127 (44), 15515-15520• DOI: 10.1021/ja0543651 • Publication Date (Web): 12 October 2005

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 10/12/2005

On the Correlation between Bond-Length Change and Vibrational Frequency Shift in Hydrogen-Bonded Complexes: A Computational Study of Y···HCl Dimers (Y = N_2, CO, BF)

Sean A. C. McDowell*,† and A. David Buckingham

Contribution from the Department of Chemistry, Lensfield Road, University of Cambridge, Cambridge CB2 1EW, England

Received July 1, 2005; E-mail: sacm1@cam.ac.uk

Abstract: The H−Cl bond-length change and the harmonic vibrational frequency shift of the H−Cl stretch on formation of the linear isoelectronic Y···H−Cl complexes (Y = N_2, CO, BF) have been determined by ab initio computations at different levels of theory. These shifts are in agreement with predictions from a model based on perturbation theory and involving the first and second derivatives of the interaction energy with respect to displacement of the H−Cl bond length from its equilibrium value in the isolated monomer. At the highest level of theory, blue shifts were obtained for BF···HCl and CO···HCl, while red shifts were obtained for FB···HCl, OC···HCl, and N_2···HCl. These vibrational characteristics are rationalized by considering the balance between the interaction energy derivatives obtained from the perturbative model. The widely believed correlation between the bond-length change and the sign of the frequency shift obtained on complexation is discussed and found to be unreliable.

1. Introduction

The hydrogen bond is probably the most important noncovalent interaction in chemistry and biology, especially as it determines the structure and behavior of biologically important systems and processes. The hydrogen bond may be considered as a relatively weak interaction between an X−H bond (where X is an element such as N, O, or F with an electronegativity greater than that of H) and an electronegative proton acceptor Y (which contains a region of high electron density); i.e., an X−H···Y interaction.[1−3] The interaction is thought to be primarily electrostatic in nature,[1−3] although it is considered by some to have a charge-transfer character[1].

An important feature of hydrogen bonding is a decrease of the X−H stretching frequency (red shift), which is usually accompanied by an elongation of the X−H bond and an increase in the infrared intensity and broadening of the spectral band associated with the X−H stretching frequency. The prevailing view is that the attractive electrostatic interaction of the electron-rich region of Y for the proton of X−H causes an elongation of the X−H bond which yields a red shift of the X−H stretch. This effect has also been attributed to charge transfer from the proton acceptor Y to (primarily) the X−H σ^* antibonding orbital of the proton donor, which causes a weakening of this bond and concomitant bond elongation.[4] The distinction between charge transfer and electronic polarization may, however, be largely illusory (see ref 5). The detection of the red shift in the IR spectrum is regarded as the "signature" of hydrogen bonding.[6]

However, growing evidence over the past few years has shown that the X−H stretching frequency can *increase* on complexation (a blue shift). It is usually observed that three features of conventional hydrogen bonds (elongation, red shift and IR intensity increase) are reversed in blue-shifting hydrogen bonds. Numerous experimental and theoretical studies of the unusual blue shifts due to hydrogen bonding have been reported in recent years,[7−24] but opinion is still divided on the nature and origin of this phenomenon.

---

† On leave from Department of Biological and Chemical Sciences, University of the West Indies, Cave Hill Campus, Bridgetown, Barbados.

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York: 1997.
(2) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford: 1999.
(3) Scheiner, S. *Hydrogen Bonding*; Oxford University Press: New York, 1997.
(4) Ratajczak, H. *J. Phys. Chem.* **1972**, *76*, 3000.
(5) Stone, A. J.; Fowler, P. W.; Buckingham, A. D. *J. Chem. Phys.* **1997**, *107*, 1030.
(6) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1715.
(7) Matsuura, H.; Yoshida, H.; Hieda, M.; Yamanaka, S.-Y.; Harada, T.; Shin-Ya, K.; Ohno, K. *J. Am. Chem. Soc.* **2003**, *125*, 13910.
(8) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **2002**, *108*, 325 and references contained therein.
(9) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253 and references contained therein.
(10) Gu, Y. L.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411.
(11) Scheiner, S.; Kar, T.; Gu, Y. L. *J. Biol. Chem.* **2001**, *276*, 9832.
(12) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784.
(13) McDowell, S. A. C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 808.
(14) McDowell, S. A. C. *J. Chem. Phys.* **2003**, *119*, 3711.
(15) McDowell, S. A. C.; Buckingham, A. D. *Spectrochim. Acta, Part A* **2005**, *61*, 1603.
(16) Herrebout, W. A.; Delanoye, S. N.; van der Veken, B. J. *J. Phys. Chem. A* **2004**, *108*, 6059.
(17) Hermansson, K. *J. Phys. Chem. A* **2002**, *106*, 4695.
(18) Pejov, L.; Hermansson, K. *J. Chem. Phys.* **2002**, *106*, 4695.
(19) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc.* **2002**, *124*, 9639.
(20) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.
(21) Wang, J.-T.; Feng, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett.* **2003**, *32*, 746.
(22) Wang, J.-T.; Feng, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chin. J. Chem.* **2004**, *22*, 642.
(23) Lu, P.; Lin, G.-Q.; Li, J.-C. *THEOCHEM* **2005**, *723*, 95.
(24) Inagaki, S.; Takeuchi, T. *Chem. Lett.* **2005**, *34*, 750.

10.1021/ja0543651 CCC: $30.25 © 2005 American Chemical Society

Some authors believe that there are no fundamental differences in the bonding characteristics of red-shifting and blue-shifting H-bonded complexes.[10,12] By contrast, Hobza and co-workers favor a two-step charge-transfer mechanism to explain the blue shift, contending that most of the electron density is transferred from the proton acceptor Y to the remote part of the proton donor (i.e., the A−X bond of the A−X−H system) rather than the antibonding σ^* orbital of the X−H bond. The electron density increase in the A−X bond leads to bond extension in that part of the system which is accompanied, in the second step, by a contraction of the X−H bond with a concomitant blue shift in the X−H stretching frequency.[8,9] In another charge-transfer based theory, Alabugin et al. attribute the blue shift to an increase in the s-character of the X−H bond (which dominates over the n(Y) $\rightarrow \sigma^*$ (X−H) hyperconjugative interaction).[20] However, as pointed out in recent papers,[21,22] the theory fails to explain the blue shift in F−He−H$\cdots N_2$ because He is incapable of rehybridization; FHeH is a metastable inert gas compound that has generated much theoretical interest as a potential candidate for experimental preparation in low-temperature matrix isolation experiments. Recent theoretical work seems to indicate that the electrostatic interaction between the proton donor and proton acceptor, along with the short-range overlap repulsion, can explain the blue shifts.[13,14,17−19,22]

A promising approach is through the application of a perturbative theory of vibrational frequency shifts (originally developed to describe solvent effects in vibrational spectroscopy[25−27]) to the prediction of the blue shifts in FArH···Rg (Rg = He, Ne, Ar, Kr) complexes.[15] The theory involves the application of first- and second-order quantum mechanical perturbation theory. The intermolecular interaction potential energy, U, is expanded as a power series in the normal mode coordinates and treated, along with the cubic anharmonicity, as a perturbation to the harmonic oscillator. The frequency shift is related to the first and second derivatives of U (U' and U''), and the relative magnitude and sign of these two derivatives determine the type and size of the frequency shift obtained. The bond-length change is proportional to $-U'$. The applicability of this perturbation theory has recently been explored.[15,16]

Even though there is no generally accepted explanation for the blue shift in hydrogen-bonded complexes, a number of views have developed over the past few years concerning certain defining characteristics of this type of hydrogen bonding and especially the relationship between the X−H bond-length change and the type of frequency shift obtained on complexation. To summarize, some of these views include the following:

(i) a necessary (but not sufficient) condition for a proton donor to be capable of forming a blue-shifting hydrogen bond is the presence of a *negative* dipole moment derivative (for the isolated proton donor) with respect to the stretching coordinate, i.e., $\partial\mu/\partial r_{XH} < 0$;[17,18]

(ii) the blue shift is accompanied by a decrease in the IR intensity of the X−H stretch; see, for example, refs 13 and 14;

(iii) the blue shift is attributed to transfer of electron density from the proton acceptor into the antibonding σ^* orbital of the remote bond(s) A−X of the proton donor A−X−H;[8,9]

(iv) the bond extension/red shift and bond compression/blue-shift correlation in hydrogen-bonded complexes is so widespread that it is safe to predict the type of X−H frequency shift (whether red or blue) from bond-length changes *only* (without the need for a time-consuming vibrational normal-mode analysis).[28]

In this paper we present ab initio computational results for a series of linear isoelectronic complexes of HCl with the proton acceptors N_2, CO and BF. We considered two different basis sets and two different levels of theory in order to assess the sensitivity of the computed properties to basis set size and the level of electron correlation. According to the results, HCl forms stable H-bonded linear complexes with the three diatomic molecules and can bind to either atom of the heteroatomic proton acceptors. Several structural and vibrational properties of the HCl complexes were computed, but the properties that are particularly interesting are the change in the H−Cl bond length and the frequency shift and IR intensity change of the H−Cl stretch on complexation, since they challenge the ideas outlined in points (i) to (iv) above. Furthermore, point (iv) raises the question of the validity of the universally accepted bond length/frequency shift correlation, which we shall explore later. The standard ab initio approach was compared with the perturbative model described above, and the theoretical methods are in good agreement.

Our study of the HCl complexes shows that $\partial\mu/\partial r_{XH} < 0$ for blue-shifting hydrogen bonds is not a necessary condition (point (i)), since HCl has a *positive* dipole moment derivative with respect to displacement of the proton and small blue shifts are obtained for BF···HCl and CO···HCl. We also found that there is an *increase* in the IR intensity of the H−Cl stretch for all of the complexes, including those that exhibit blue shifts (point (ii)). The charge-transfer mechanism proposed by Hobza and co-workers (point (iii)) cannot be used to explain the blue shift in BF···HCl and CO···HCl, since HCl is a diatomic and therefore has only *one* bond into which electron density from the bonding partner can be transferred. We also show that, at the highest level of theory employed in our study, a bond extension and a blue shift are obtained for CO···HCl, which invalidates point (iv) and calls into question the accepted correlation between bond length and frequency shift. The perturbative model shows that, in principle, it is possible for a blue shift to be obtained with a bond extension.

It should be noted that there are instances in the literature where there are apparent violations of the bond length/frequency shift paradigm, which in itself makes point (iv) a hazardous proposal. However, for the cases that the authors are aware of and which we shall discuss now, the results are dubious because the basis set/level of theory was inadequate or, more importantly, the optimized structures reported do *not* represent true minima. For example, Govender and Ford report an MP2/6-311++G-(d,p) structure for $H_2S\cdots HF$ (an S−H···F type interaction) in which there is an extension of 0.0003 Å and a blue shift of 3.3 cm^{-1} for the S−H stretch.[29] We have repeated this calculation and agree with their findings. However, the optimized $H_2S\cdots$HF structure is *not* a minimum (having one imaginary frequency of 61.6i cm^{-1}). Similarly, Lignell et al. report an optimized structure for HHeF in an octahedral Xe cage (denoted HHeF···

---

(25) Buckingham, A. D. *Proc. R. Soc. London, Ser. A* **1958**, *248*, 169.
(26) Buckingham, A. D. *Proc. R. Soc. London, Ser. A* **1960**, *255*, 32.
(27) Buckingham, A. D. *Trans. Faraday. Soc.* **1960**, *56*, 753.
(28) Zierkiewicz, W.; Jurečka, P.; Hobza, P. *ChemPhysChem* **2005**, *6*, 609.
(29) Govender, M. G.; Ford, T. A. *THEOCHEM* **2003**, *630*, 11.

Table 1. Molecular Properties for the Optimized Structures of HCl Computed at Three Different Levels of Theory[a]

calculated property	MP2/6-311++G(2d,2p)	QCISD/6-311++G(2d,2p)	QCISD/6-311++G(3df,3pd)
r_e/Å	1.2705	1.2722	1.2740
μ/D	1.1831	1.1482	1.0727
$\partial\mu/\partial r$/D Å^{-1}	1.098	0.911	0.959
ω_e/cm^{-1}	3002.2	2964.0	3025.4
I/km mol^{-1}	52	36	40
B_e/cm^{-1}	10.649	10.620	10.591
a	−2.423	−2.484	−2.343

[a] r_e is the equilibrium bond length, μ is the molecular dipole moment, $\partial\mu/\partial r$ is the dipole moment derivative with respect to displacement of the H−Cl bond, ω_e is the harmonic vibrational stretching frequency, I is the intensity of the HCl fundamental vibration, B_e is the rotational constant, and a is the cubic anharmonicity

Table 2. Molecular Properties for the Optimized Structures of N$_2$, CO, and BF Computed at Three Different Levels of Theory[a]

calculated property	MP2/6-311++G(2d,2p)	QCISD/6-311++G(2d,2p)	QCISD/6-311++G(3df,3pd)
N$_2$ r_e/Å	1.1139	1.0982	1.0975
μ/D	0	0	0
ω_e/cm^{-1}	2171.2	2383.2	2404.5
CO r_e/Å	1.1379	1.1311	1.1285
μ/D	0.2694	0.0914	0.0812
ω_e/cm^{-1}	2113.5	2176.8	2196.0
BF r_e/Å	1.2684	1.2706	1.2645
μ/Å	0.9455	0.7907	0.8348
ω_e/cm^{-1}	1396.2	1385.5	1399.8

[a] r_e is the equilibrium bond length, μ is the dipole moment, and ω_e is the harmonic vibrational stretching frequency. For CO and BF, the positive dipole moment has the sense $C^{-}O^{+}$ and $B^{-}F^{+}$, respectively

Xe$_6$) for which a large blue shift of 74 cm^{-1} and a H−He bond extension of 0.002 Å were obtained;[30] again, this structure is not a minimum, having low imaginary frequencies (<10i cm^{-1}). A recent paper by Lu et al.[23] highlights the problem of deducing the frequency shift from the bond length change. They found that MP2 and B3LYP both predict red shifts of the C−H stretch in F$_3$C−H···NH$_3$ using a 6-311++G(d,p) basis set. However, MP2 predicts a small bond contraction, while B3LYP predicts a bond extension.

We have not compared our perturbation theoretical frequency shift values with experiment, since it would be necessary to perform a more detailed analysis involving taking the average of the derivatives of U over the intermolecular stretching and bending vibrational modes in the complex. Our purpose in the present work is to compare the performance of the perturbation theory model with the standard ab initio approach in order to clarify the bond length/frequency shift paradigm and to gain insight into the origin of the unusual blue shift.

A detailed exposition of the perturbative model and its application to some H-bonded complexes can be found in ref 15; only a brief outline will be given here. The perturbative model essentially approximates the complexation-induced frequency shift, $\Delta\omega$, for the fundamental absorption band of a perturbed diatomic oscillator as[27]

$$hc\Delta\omega = (B_e/\omega_e)(U'' - 3aU') \tag{1}$$

where B_e is the rotational constant $h/(8\pi^2 mcr_e^2)$, m the reduced mass, $c\omega_e$ the frequency of the harmonic oscillator, and a the cubic anharmonic constant. The constants B_e, ω_e, and a are all determined by ab initio computations, while U' and U'' are determined numerically by ab initio single-point energy computations on HCl and Y···HCl. The first term in eq 1 arises from a shift in the harmonic force constant due to the intermolecular interaction, while the second term, which is proportional to the bond stretching force, $-U'$, arises from a change in the equilibrium bond length which will influence the vibrational frequency if the vibration is anharmonic (i.e., if $a \neq 0$) .

The bond length change of the oscillator (Δr) can also be determined by the model, since it is related to U' by the equation[26]

$$\Delta r = -2B_e r_e U'/(hc\omega_e^{\,2}) \tag{2}$$

This equation, taken with eq 1, implies that the shift $\Delta\omega$ will not always reflect the bond-length change; this is illustrated by the computational results for the CO···HCl dimer which are presented later.

2. Computational Procedure

All ab initio calculations were performed using the Gaussian 03 suite of programs[31] using two different basis sets, 6-311++G(2d,2p) and 6-311++G(3df,3pd), and two different levels of theory, MP2 and QCISD. The monomers and complexes were optimized to stable linear structures. The molecular properties of HCl and of the proton acceptors, N$_2$, CO, and BF, are shown in Tables 1 and 2, respectively. For the heteroatomic proton acceptors, CO···HCl, OC···HCl, BF···HCl, and FB···HCl were all found to be stable.

Harmonic vibrational frequencies were calculated for the H−Cl stretch in the linear dimers (ω^{complex}) and for the isolated HCl molecule (ω_e) by analytic second derivatives, which confirms that the optimized structures are true minima (no imaginary frequencies). The frequency shift ($\Delta\omega$) is then approximated by $\Delta\omega = \omega^{\text{complex}} - \omega_e$. Interaction energies were computed with and without correction for the zero-point vibrational energy (ZPE). The relevant properties for the five complexes

---

(30) Lignell, A.; Khriachtchev, L.; Räsänen, M.; Pettersson, M. *Chem. Phys. Lett.* **2004**, *390*, 256.

(31) M. J. Frisch et al. *Gaussian 03*, revision B.05; Gaussian Inc.: Pittsburgh, PA, 2003.

Table 3. Optimized Geometry, Dipole Moment, Harmonic Vibrational Frequency (ω_e) of the H−Cl Stretching Mode, and Dissociation Energy without (D_e) and with Zero-Point Vibrational Energy Correction (D_0) with Respect to the Isolated Monomers, in the Optimized Linear Y···HCl Complexes (Y = N_2, CO, BF) at the MP2/6-311++G(2d,2p) Level of Theory[a]

property	N–N···H–Cl	C–O···H–Cl	O–C···H–Cl	B–F···H–Cl	F–B···H–Cl
r(Cl−H)/Å	1.2727	1.2712	1.2757	1.2706	1.2836
R(H···Y)[b]/Å	2.3294	2.3272	2.3232	2.3651	2.3248
μ/D	1.538	1.2071	1.9621	0.4705	2.9389
D_e/kJ mol^{-1}	7.93	5.58	10.64	3.56	16.74
D_0/kJ mol^{-1}	3.11	2.02	5.69	0.76	11.32
ω(HCl)/cm^{-1}	2978.6	2999.4	2930.6	3006.9	2808.1
$I^{\text{complex}}/I^{\text{monomer}}$	3.67	2.85	5.75	2.13	10.9

[a] Only the high-frequency intramolecular vibrational mode is shown. The change in the IR intensity of the HCl stretch on complexation ($I^{\text{complex}}/I^{\text{monomer}}$) is also shown. [b] R(H···Y) represents the distance between the H atom and the atom of the proton acceptor (N_2, CO, BF) which is directly bonded to it.

Table 4. Optimized Geometry, Dipole Moment, Harmonic Vibrational Frequency (ω_e) of the H−Cl Stretching Mode, and Dissociation Energy with (D_e) and without Zero-Point Vibrational Energy Correction (D_0) with Respect to the Isolated Monomers, in the Optimized Linear Y···HCl Complexes (Y = N_2, CO, BF) at the QCISD/6-311++G(2d,2p) Level of Theory

property	N–N···H–Cl	C–O···H–Cl	O–C···H–Cl	B–F···H–Cl	F–B···H–Cl
r(Cl−H)/Å	1.2734	1.2727	1.2753	1.2723	1.2798
R(H···Y)[a]/Å	2.4274	2.3692	2.4242	2.3746	2.4466
μ/D	1.456	1.3463	1.6612	0.6028	2.594
D_e/kJ mol^{-1}	6.39	5.49	8.32	3.91	12.89
D_0/kJ mol^{-1}	1.89	1.93	3.79	0.98	7.81
ω(HCl)/cm^{-1}	2958.6	2968.4	2929.2	2971.7	2860.2
$I^{\text{complex}}/I^{\text{monomer}}$	3.58	3.11	5.3	2.39	9.3

[a] R(H···Y) represents the distance between the H atom and the atom of the proton acceptor (N_2, CO, BF) which is directly bonded to it.

Table 5. Optimized Geometry, Dipole Moment, Harmonic Vibrational Frequency (ω_e) of the H−Cl Stretching Mode, and Dissociation Energy with (D_e) and without Zero-Point Vibrational Energy Correction (D_0) with Respect to the Isolated Monomers, in the Optimized Linear Y···HCl Complexes (Y = N_2, CO, BF) at the QCISD/6-311++G(3df,3pd) Level of Theory

property	N–N···H–Cl	C–O···H–Cl	O–C···H–Cl	B–F···H–Cl	F–B···H–Cl
r(Cl−H)/Å	1.2749	1.2744	1.2768	1.2736	1.2815
R(H···Y)[a]/Å	2.3823	2.3413	2.4142	2.352	2.4256
μ/D	1.4226	1.3124	1.605	0.4964	2.6124
D_e/kJ mol^{-1}	7.06	5.82	9.01	3.49	13.43
D_0/kJ mol^{-1}	2.53	2.09	4.47	0.87	8.27
ω(HCl)/cm^{-1}	3019.6	3028.2	2989.8	3034.7	2918.1
$I^{\text{complex}}/I^{\text{monomer}}$	3.68	3.15	5.05	2.38	9.15

[a] R(H···Y) represents the distance between the H atom and the atom of the proton acceptor (N_2, CO, BF) which is directly bonded to it.

Table 6. The H−Cl Bond-Length Change on Complexation (Δr) and the Vibrational Frequency Shift of the H−Cl Stretch ($\Delta\omega$) for HCl in the Y···HCl (Y = N_2, CO, BF) Complexes at Various Levels of Theory. $\Delta\omega = \omega(\text{HCl})^{\text{complex}} - \omega_e^{\text{monomer}}$

calculated property	MP2/ 6-311++G(2d,2p)	QCISD/ 6-311++G(2d,2p)	QCISD/ 6-311++G(3df,3pd)
(N_2...HCl) Δr/Å	0.0023	0.0012	0.0010
$\Delta\omega$/cm^{-1}	−23.6	−5.4	−5.8
(BF···HCl) Δr/Å	0.0001	0.00005	−0.0003
$\Delta\omega$/cm^{-1}	+4.7	+7.7	+9.3
(FB···HCl) Δr/Å	0.0132	0.0076	0.0075
$\Delta\omega$/cm^{-1}	−194.1	−103.8	−107
(CO···HCl) Δr/Å	0.0008	0.0005	0.0004
$\Delta\omega$/cm^{-1}	−2.8	+4.4	+ 2.8
(OC···HCl) Δr/Å	0.0052	0.0030	0.0028
$\Delta\omega$/cm^{-1}	−71.6	−34.8	−35.6

at the MP2/6-311++G(2d,2p), QCISD/6-311++G(2d,2p), and QCISD/6-311++G(3df,3pd) levels of theory are given in Tables 3−6. The interaction energies may be affected by the basis set superposition error (BSSE), which is usually corrected by the counterpoise method of Boys and Bernardi.[32] However, MP2 has a tendency to overcorrect for the BSSE so we do not correct the interaction energies; we are using moderately large basis sets and so do not believe that the BSSE will significantly affect the conclusions arrived at from our study.

To calculate the frequency shift of the H−Cl stretch and the HCl bond-length change in the dimers using the perturbative model, we first assume that the proton acceptor remains stationary during the ground-state oscillations of HCl in the dimer and also that its bond length remains fixed at its equilibrium value in the isolated molecule. The interaction potential energy, U, was determined by ab initio supermolecule calculations on the complex. After optimization of the Y···HCl complex, the Y to Cl separation is fixed at its equilibrium value in the complex. The optimized H−Cl bond length in the isolated molecule is computed and taken as r_e in the complex. For each increment Δ of the H−Cl bond from its r_e value, retaining the Y···HCl linear geometry, the interaction energy is determined as $U = E_{\text{Y}\cdots\text{HCl}} - E_{\text{HCl}} - E_{\text{Y}}$, where all three quantities are total energies. The frequency shift can now be computed using eq 1 and is compared with the value obtained via a standard ab initio analytic second derivatives calculation, while the bond-length change can be determined via eq 2 and compared with the ab initio result. These results for QCISD/6-311++G(3df,3pd) are shown in Table 7.

Table 7. The Y···H−Cl (Y = N$_2$, CO, BF) Interaction Potential Energies, *U*, as Calculated at the QCISD/6-311++G(3df,3pd) Level of Theory[a]

property	N–N···H–Cl	B–F···H–Cl	F–B···H–Cl	C–O···H–Cl	O–C···H–Cl
$U(r_e+\Delta)$/cm^{-1}	−602.743	−279.648	−1213.715	−489.731	−790.159
$U(r_e)$/cm^{-1}	−590.275	−286.531	−1109.732	−485.875	−750.159
$U(r_e-\Delta)$/cm^{-1}	−576.569	−290.119	−1024.6	−478.973	−715.964
$U'(r_e)$/cm^{-1}	−333.45	133.4	−2409.23	−137.06	−945.22
$U''(r_e)$/cm^{-1}	803.58	2138.6	−12237.5	1977.06	−3299.8
$-3aU'(r_e)$/cm^{-1}	−2343.8	937.65	−16934.5	−963.39	−6643.9
$\Delta\omega^{\mathrm{model}}$/cm^{-1}	−5.4	+10.8	−102	+3.6	−34.8
$\Delta\omega^{\mathrm{ab\ initio}}$/cm^{-1}	−5.8	+9.3	−107	+2.8	−35.6
$\Delta r^{\mathrm{model}}$/Å	0.000 98	−0.0004	0.0071	0.00040	0.0028
$\Delta r^{\mathrm{ab\ initio}}$/Å	0.000 99	−0.0003	0.0075	0.000 42	0.0028

[a] The increment Δ corresponds to an increase in the H−Cl bond length (from its r_e value in the isolated HCl molecule), keeping *R*(Y···Cl) fixed at the equilibrium value in the linear optimized complex; the Y bond length is also fixed at its r_e value in the isolated monomer. Derivatives of *U* with respect to the dimensionless parameter $\xi = (r - r_e)/r_e$, U' and U'', are then determined by finite differences (see main text). For each increment $\Delta = 0.05$ Å, the interaction energy is determined as $U = E(\mathrm{Y\cdots HCl}) - E(\mathrm{HCl}) - E(\mathrm{Y})$. A comparison of ab initio frequency shifts, $\Delta\omega$ ($= \omega^{\mathrm{complex}} - \omega_e$), of the H−Cl stretch in Y···HCl with predictions from the perturbative model are shown. i.e., $\Delta\omega^{\mathrm{model}} = (B_e/\omega_e)(U'' - 3aU')$. The bond-length change predicted by the model is given by $\Delta r^{\mathrm{model}} = (-2B_e r_e U')/\omega_e^2$ and is also compared with the ab initio result.

3. Discussion

Table 1 shows that HCl has a positive dipole moment derivative $\partial\mu/\partial r$ (0.959 D Å^{-1} at QCISD). Of the isoelectronic proton acceptors given in Table 2, N$_2$ does not have a permanent dipole moment, while CO and BF have a dipole moment whose sense is C$^-$O$^+$ and B$^-$F$^+$, respectively.

The five complexes, N$_2$···HCl, OC···HCl, CO···HCl, FB···HCl, and BF···HCl, are all stable with respect to the constituent monomers. An important source of the attraction is the dipole−quadrupole electrostatic interactions. The dipole−dipole electrostatic interaction is not strong enough in the CO and BF complexes to prevent CO···HCl and BF···HCl from being stable, although these complexes have a smaller interaction energy than the complexes with the dipoles acting in parallel (i.e., O$^+$C$^-$···HCl and F$^+$B$^-$···HCl); see Tables 3−5. Induction and dispersion forces are also expected to make a substantial contribution to the binding energy of these dimers.

The FB···HCl dimer is the most stable with a binding energy D_e of 13.4 kJ mol^{-1} at QCISD/6-311+G(3df,3pd), while the BF···HCl dimer is the least stable with a binding energy of 3.5 kJ mol^{-1}. The order of energetic stability for all three computational levels is FB···HCl > OC···HCl > N$_2$···HCl > CO···HCl > BF···HCl with the zero-point vibrational energy correction being significant, especially for BF···HCl. This is also the order for the total dipole moment and the IR intensity enhancement of the H−Cl stretch on complexation. The larger binding energies and dipole moments for FB···HCl and OC···HCl reflect the favorable orientation of the individual monomer dipole moments (which would also yield a larger induction energy contribution to the intermolecular potential). Interestingly, the relative magnitude of the intermolecular H···Y separation varies as we go from Table 3 to Table 5, indicating the sensitivity of this physical parameter to the basis set and level of theory.

Table 6 shows that the H−Cl bond-length changes and frequency shifts are sensitive to the level of electron correlation used. The increase in the basis set size from 6-311++G(2d,2p) to 6-311++G(3df,3pd) at QCISD is much less sensitive, and there is good agreement between the values, except for BF···HCl, in which a negligible extension (0.000 05 Å) of the H−Cl bond is obtained with the 6-311++G(2d,2p) basis set, whereas a small contraction (by 0.0003 Å) is obtained with 6-311++G(3df,3pd). At MP2, a blue shift was predicted for BF···HCl, while red shifts were predicted for N$_2$···HCl, FB···HCl, CO···HCl, and OC···HCl. However, increasing the level of theory from MP2 to QCISD diminishes the red shifts and increases the blue shift in the Y···HCl dimers. For CO···HCl, the red shift of 2.8 cm^{-1} at MP2 changes to blue shifts of 4.4 and 2.8 cm^{-1} at QCISD/6-311++G(2d,2p) and QCISD/6-311++G(3df,3pd), respectively. The QCISD/6-311++G(3df,3pd) method is assumed to be the most accurate theoretical method used in our study and yields frequency shifts of −5.8 and −35.6 cm^{-1} for N$_2$···HCl and OC···HCl, respectively, to be compared with the experimental results of −8.0 and −34.2 cm^{-1} due to McKellar and Lu.[33]

The correlation between H−Cl bond-length change and frequency shift can be seen from the QCISD/6-311++G(3df,3pd) results in Table 6. Here a red shift and an extension of the H−Cl bond are obtained for N$_2$···HCl, FB···HCl, and OC···HCl, while a blue shift and a compression of the H−Cl bond is obtained for BF···HCl. Surprisingly, a blue shift accompanied by a H−Cl bond *extension* is predicted for CO···HCl.

Table 7 shows that both the frequency shift and bond-length changes predicted by the perturbative model are in good agreement with the full ab initio supermolecule calculations. The bond-length change depends on U', while the frequency shift depends on both U' and U''. Therefore, the relative contributions of U' and U'' determine the sign and magnitude of the frequency shift, while the *sign* of U' determines what type of bond-length change is obtained (if $U' < 0$ there is a bond extension, and if $U' > 0$, a bond contraction). Referring to the QCISD values in Table 7, we get four different possibilities for the Y···HCl complexes:

(a) red shift and bond extension in FB···HCl and OC···HCl, since both U' and U'' contributions < 0;

(b) blue shift and bond contraction in BF···HCl, since both U' and U'' contributions > 0;

(c) red shift and bond extension in N$_2$...HCl, since the U' contribution < 0, $U'' > 0$, but the U' contribution > that of U'';

(d) blue shift and bond extension in CO···HCl, since $U' < 0$, $U'' > 0$, but the U' contribution is less than that of U''. This is the anomalous situation and should be compared with (c) above.

---

(32) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(33) McKellar, A. R. W.; Lu, Z. *J. Mol. Spectrosc.* **1993**, *161*, 542.

To sum up, the results shown in the tables indicate the following:

(i) It is not necessary for $\partial\mu/\partial r_{XH} < 0$ for a proton donor to be capable of forming a blue-shifted hydrogen bond, since blue shifts were obtained for BF···HCl and CO···HCl, even though $\partial\mu/\partial r_{XH} > 0$ for HCl.

(ii) It is possible for a blue shift to be consistent with an *increase* in the IR intensity, since IR intensity enhancements of the H−Cl stretch were obtained for all complexes, including the blue-shifting complexes BF···HCl and CO···HCl (Tables 5 and 6).

(iii) The charge-transfer mechanism proposed by Hobza and co-workers cannot explain the blue shifts obtained, since HCl is a diatomic.

(iv) Prediction of the sign of the frequency shift from the bond-length change is unreliable because either or both properties may be inaccurate if the level of theory is too low or if the optimized structure does not represent a true minimum. It is essential that a vibrational analysis be performed after optimization to confirm that a true minimum is obtained.

(v) Finally, the perturbative model provides fair estimates of the vibrational frequency shifts and bond-length changes occurring in the Y···HCl complexes that compare well with full ab initio calculations. The relative contributions of U' and U'' to the frequency shift are useful in rationalizing the blue shift.

Supporting Information Available: Complete ref 31. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0543651