Blue-Shifting or Red-Shifting Hydrogen Bonding? Predictions for Haloform Complexes with Dimethyl Ether on the Basis of Perturbation Theory

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Frequency shifts of the C−H stretching mode, ν_1, of the haloforms CHF_3, $CHClF_2$, $CHCl_2F$, and $CHCl_3$ because of complexation with dimethyl ether have been calculated from an ab initio interaction potential between the two molecules, using a perturbative approach. The shift is described as a sum of two terms, a first due to a stiffening of the C−H bond, the second due to the attractive or repulsive nature of the interaction of the C−H bond with the Lewis base. For CHF_3 through $CHCl_2F$, both terms are positive, resulting in an overall blue shift of ν_1; for the complex with $CHCl_3$, the attractive interaction with the Lewis base causes a red shift which is larger than the blue shift because of the stiffening of the C−H bond, resulting in a small overall red shift. The calculated results are compared with experimental literature data on these complexes.

1. Introduction

To describe solvent influences on vibrational frequencies of a solute, a model was proposed by D. Buckingham a considerable number of years ago.[1−3] The essence of the model is that apart from the intramolecular potential the solvent causes an additional potential U to which the solute's atoms are subjected. The potential U is developed in a truncated Taylor series in the solute's normal coordinates, retaining only first- and second-order terms. Subsequently, the potential U is used as a perturbation in a second-order perturbation approach. To evaluate the possible sign combinations of the first- and the second-order terms of U, the simple case of a diatomic molecule X−H of which the hydrogen atom interacts with a third atom Y was used. The similarity of the latter to a hydrogen bond is obvious, and this model has been used[4,5] to interpret the hydrogen fluoride vibrational frequency shift in the van der Waals complexes Ne·HF, Ar·HF, N_2·HF, and CO·HF. More recently,[6,7] the model was taken up in the description of the solvent influences caused by liquefied N_2, CO, and CO_2 on the solute CHF_3. In that publication, the variation of the solvent shift on $\nu_1^{CHF_3}$ was qualitatively explained in terms of changes in the interaction potential U.

In this study, we take this renewed interest in Buckingham's model a step further by applying it quantitatively to a series of weak complexes in which a C−H bond is hydrogen bonded to the electron donor oxygen atom of dimethyl ether. The Lewis acids in this series are CHF_3, $CHClF_2$, $CHCl_2F$, and $CHCl_3$. Infrared spectra have shown[8] that in that series the hydrogen bond gradually changes from blue shifting in the fluoroform complex to red shifting in the chloroform complex. The aim of the study, therefore, is to relate the evolution of the hydrogen bond in the series to the changes in the first- and second-order derivatives of the interaction potential U_3, in an attempt to shed further light on the still elusive phenomenon of blue shifting hydrogen bonding.[9−41]

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2. Computational Details

Ab initio calculations were performed at the MP2=FULL/6-31++G(d,p) level, using Gaussian03.[42] During all calculations, corrections for basis set superposition error (BSSE) were taken into account using the CP-corrected gradient techniques proposed by Simon and Dannenberg.[43,44]

3. Results

3.1. The Model. The model applied here is a minor adaptation of the one proposed by Buckingham for a diatomic molecule in interaction with a solvent molecule.[1−3] The use of a diatomic approximation is justified for the Lewis acids studied here in view of the isolated nature of the C−H stretching involved.

The C−H stretching in the momomer proton donor is described by the Hamiltonian H_a:

$$H_a = H_h + k_{3a}Q_1^{\,3} + k_{4a}Q_1^{\,4} \tag{1}$$

in which H_h is the harmonic oscillator Hamiltonian, containing the harmonic potential $k_{2a}Q_1^2$, and k_{3a} and k_{4a} are the diagonal cubic and quartic force constants, in the Nielsen notation,[45] expressed using the dimensionless normal coordinate Q_1 for the C−H oscillator. The influence of the formation of a complex on the C−H stretching is described by a perturbing potential $U(Q_1)$, leading to a Hamiltonian H_t which, when using a series expansion in the Nielsen notation and for $U(Q_1)$ truncated after the third-order term, results in

$$H_t = H_a + U(Q_1) = H_a + \sum_{n=1}^{3} k_{nu}Q_1^{\,n} \tag{2}$$

The eigenfunctions $|a,i\rangle$ of H_a and $|t,i\rangle$ of H_t, with i the energy level counter, are developed in a harmonic oscillator base. The fundamental frequencies $\nu_{monomer}$ and $\nu_{complex}$ for the oscillators H_a and H_t can then be expressed as

$$\nu_{monomer} = \langle a,1|H_a|a,1\rangle - \langle a,0|H_a|a,0\rangle \qquad (3)$$

$$\nu_{complex} = [\langle t,1|H_a|t,1\rangle - \langle t,0|H_a|t,0\rangle]$$

$$+ \sum_{n=1}^{3} k_{nu}[\langle t,1|Q_1^{\ n}|t,1\rangle - \langle t,0|Q_1^{\ n}|t,0\rangle]$$

$$= \nu_o + \sum_{n=1}^{3} \Delta\nu_n^{\ t} \qquad (4)$$

Equation 4 expands the complex frequency into a series, the final three terms of which measure the contributions of each of the terms of the perturbation potential $U(Q_1)$. It must be stressed that the first term of this series, ν_o, is not equal to the monomer frequency, as is clear from comparison with eq 3. This hampers the use of this series in the interpretation of the complexation shifts. When the perturbing potential U is sufficiently small, this can be overcome by using the $|a,i\rangle$ as a first approximation to the $|t,i\rangle$, so that $\nu_{complex}$ can be written as

$$\nu_{complex} = \nu_{monomer} + \sum_{n=1}^{3} k_{nu}[\langle a,1|Q_1^{\ n}|a,1\rangle - \langle a,0|Q_1^{\ n}|a,0\rangle]$$

$$= \nu_{monomer} + \sum_{n=1}^{3} \Delta\nu_n^{\ a} \qquad (5)$$

3.2 Calculations. The calculation of the complexation shifts $\Delta\nu_k^{\ a}$ requires knowledge of the anharmonicity constants k_{3a} and k_{4a} and of the perturbation potential $U(Q_1)$. The anharmonicity constants were calculated as follows. In a first step, the equilibrium geometry of the haloform was optimized using the tight convergence criteria, and the eigenvector for the CH stretching mode was calculated in the harmonic approximation. To reduce numerical errors, the displacements of all atoms were calculated using five decimal digits, by adding the FREQ=HPMODES option of Gaussian.[42] The resulting eigenvector was used to calculate the Cartesian coordinates of the atoms for a set of 51 equidistant values of Q_1 between -2.5 and $+2.5$, with a unit of Q_1 corresponding to a displacement of approximately 0.1 Å of the hydrogen atom. This range covers the region of significant values of the wave functions of the ground and the first excited states. Subsequently, for each value of Q_1, the single-point energy $E(Q_1)$ was calculated. The force constants k_{ia} were obtained from a nth order polynomial $F(Q_1)$ that was least-squares fitted to the $E(Q_1)$:

$$F(Q_1) = F_0 + \sum_{i=1}^{n} k_{ia}Q_1^{\ i} \qquad (6)$$

In this expression, F_0 represents the equilibrium energy of the haloform, which should equal the value of $E(0)$ obtained from the ab initio geometry optimization. Values of $F_0 - E(0)$ for fourth- and fifth-order polynomials equal $-135(125)$ and $54(12)$ cm^{-1}, while for a sixth-order polynomial the residual has decreased to $2(1)$ cm^{-1}. Calculations for $n = 7$ and 8 did not improve the residual and resulted in negligible values, about 10^{-15}–10^{-16} cm^{-1}, for k_{7a} and k_{8a}. Therefore, for subsequent analysis, the results for the sixth-order polynomial were adopted. These, together with their 2σ uncertainties, are collected in Table 1.

For the least-squares curve to correctly represent the vibrational potential, it must reach its minimum at $Q_1 = 0$. This leads to the condition that k_{1a} must be zero. Also, the quadratic

TABLE 1: Expansion Coefficients k_{na}, in cm^{-1}, and Goodness-of-the-Fit Parameters, in cm^{-1}, for the CH Stretching Fundamental in CHF$_3$, CHClF$_2$, CHCl$_2$F, and CHCl$_3$[a,b]

	CHF$_3$	CHClF$_2$	CHCl$_2$F	CHCl$_3$
$F_0 - E(0)$	2.0 (11)	2.0 (10)	2.0 (10)	2.0 (11)
k_{1a}	−6 (2)	−6 (2)	−5 (2)	−5 (2)
k_{2a}	1630.5 (9)	1622.4 (9)	1619.6 (9)	1619.3 (9)
k_{3a}	−333.5 (3)	−335.7 (2)	−337.9 (3)	−339.5 (3)
k_{4a}	47.6 (2)	48.2 (2)	48.6 (2)	48.9 (2)
k_{5a}	−5.4 (1)	−5.6 (1)	−5.6 (1)	−5.6 (1)
k_{6a}	0.3 (1)	0.3 (1)	0.3 (1)	0.4 (1)
$\omega_1 - 2k_{2a}$	10.9 (18)	10.8 (18)	11.0 (17)	11.1 (16)

[a] The harmonic frequencies ω_1 are 3271.9 cm^{-1} (CHF$_3$), 3255.6 cm^{-1} (CHClF$_2$), 3250.2 cm^{-1} (CHCl$_2$F), and 3249.7 cm^{-1} (CHCl$_3$). [b] The cubic force constants obtained by using the freq = anharm keyword in Gaussian03 are −335.1 cm^{-1} (CHF$_3$), −337.7 cm^{-1} (CHClF$_2$), −339.6 cm^{-1} (CHCl$_2$F), and −341.3 cm^{-1} (CHCl$_3$); the ab initio quartic force constants are 45.6 cm^{-1} (CHF$_3$), 46.2 cm^{-1} (CHClF$_2$), 46.7 cm^{-1} (CHCl$_2$F), and 46.9 cm^{-1} (CHCl$_3$).

force constant k_{2a} and the harmonic frequency ω_1 obtained from the harmonic ab initio force field should obey the relation $2k_{2a} = \omega_1$.

The results in Table 1 show that the values of k_{1a} and $\omega_1 - 2k_{2a}$ are very small, certainly when compared with the range of $F(Q_1)$ values covered. The k_{2a}, for instance, typically deviate by less than 0.4% from $\omega_1/2$. This suggests that $F(Q_1) - E_0$ is a sufficiently accurate representation of the Q_1 vibrational potential. This conclusion is corroborated by the similarity of the k_{3a} values for CHF$_3$ and CHClF$_2$ with cubic force constants reported in the literature[7,46,47] and by the agreement of the present values of k_{3a} and k_{4a} with the ab initio cubic and quartic force constants derived using the finite difference algorithm in Gaussian03,[42] which are given in a footnote to Table 1.

A final remark concerns the trend in the deviations of k_{1a} and k_{2a} from their expected values. Table 1 indicates that the trends are systematic: for all haloforms k_{1a} has a small negative value, and k_{2a} is underestimated, for all haloforms by a similar amount. We have not pursued interpretations of these trends.

The eigenvalues and eigenvectors of the anharmonic Hamiltonian H_a were obtained from perturbation theory using a harmonic oscillator basis. Second- to fourth-order terms of $F(Q_1)$ were considered in the perturbation calculation. Inclusion of the fourth-order term is essential, as this term starts to contribute considerably at values of Q_1 where the wave functions of interest are far from converged. Because the values of k_{5a} and k_{6a} are small, the contributions of the corresponding terms in the potential have significant values only for larger values of Q_1 where the wave functions are very nearly converged. As a consequence, these terms have very minor influences on the calculated frequencies and have for the further analysis been neglected. The number of basis functions used was set to 20, ensuring that at least the lower 10 eigenvalues were converged.

In the perturbing potential $U(Q_1)$, Q_1 is the normal coordinate of the unperturbed problem, that is, of the monomer haloform. This requires that the haloform moiety in the complex must be treated with the structure of the isolated monomer and not with its structure in the global minimum of the complex. Data on $U(Q_1)$ were, therefore, obtained in the following way. In a first calculation on each complex, the haloform was held rigidly in the structure corresponding to $Q_1 = 0$, and the other structural parameters were optimized using Gaussian03.[42] Then, with the structural parameters of the rest of the complex held rigidly,

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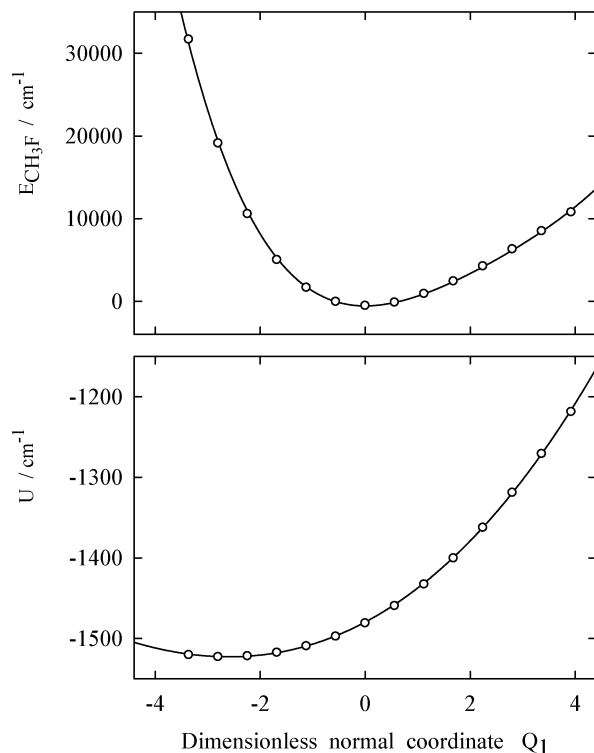*J. Phys. Chem. A, Vol. 108, No. 28, 2004* **6061**

Figure 1. Total potential energy (top) and intermolecular perturbation potential $U(Q_1)$ (bottom) as function of the dimensionless normal coordinate Q_1 of CHF$_3$ for its complex with dimethyl ether. The circles represent the calculated data. The solid lines were calculated from a least-squares sixth-order polynomial for the total potential energy and from a third-order polynomial for $U(Q_1)$.

the ab initio energy of the complex was calculated for haloform structures corresponding to a series of 18 equidistant Q_1 values in the range from -4.1 to 4.6, with the haloform center of mass kept at a constant distance to the DME moiety. This results in a series of energies of the complex $E_{com}(Q_1)$ from which the perturbing potential $U(Q_1)$ was calculated as

$$U(Q_1) = E_{com}(Q_1) - E_{halo}(Q_1) - E_{DME}(0) \qquad (7)$$

in which $E_{halo}(Q_1)$ is the energy of the monomer haloform with structure corresponding to the chosen value of Q_1, and $E_{DME}(0)$ is the energy of monomer DME calculated with the structure taken from the complex as optimized in the $Q_1 = 0$ calculation. Apart from obvious expansions needed to account for the polyatomic nature of the proton donors, this approach is similar to the one described for the HF-complexes of CO and N$_2$.[4]

As an illustration, in Figure 1 the perturbation $U(Q_1)$ (lower panel) and $E_{com}(Q_1)$ (top panel) are given as function of Q_1 for DME·CHF$_3$. For the interval of Q_1 between -2 and $+2$, in which the larger amplitudes of the vibrational wave functions for ground and first excited states are localized, $U(Q_1)$ varies by ± 150 cm^{-1}, while $E_{com}(Q_1)$ varies by ± 7500 cm^{-1}. This shows that $U(Q_1)$ may indeed be treated as a perturbation. For the other complexes, the $U(Q_1)$ are collected in Figure 2. For each complex, a third-order polynomial was fit to $U(Q_1)$. These are shown as solid lines in Figures 1 and 2. The expansion coefficients k_{nu} of the polynomials have been collected in Table 2.

4. Discussion

The absolute values of k_{3a} are much larger than those of k_{1u} and k_{3u}. As a consequence, the anharmonic characteristics of
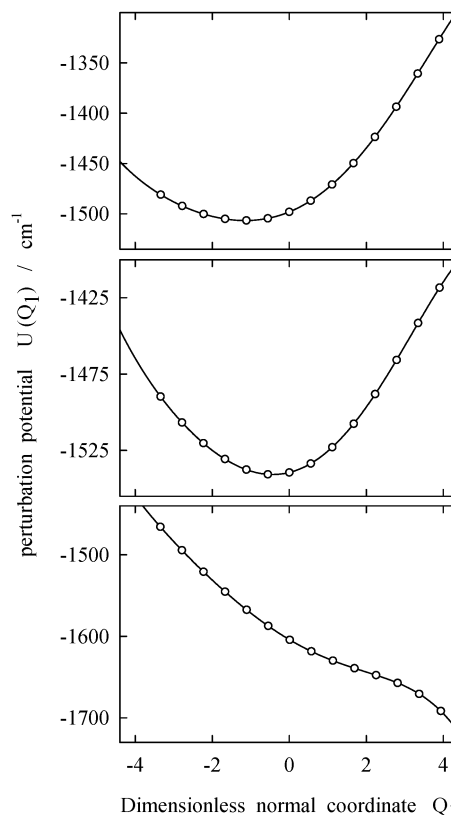

Figure 2. Intermolecular perturbation potential $U(Q_1)$ for DME·CHClF$_2$ (top), DME·CHCl$_2$F (middle), and DME·CHCl$_3$ (bottom) as function of the haloform dimensionless normal coordinate Q_1. The circles represent the calculated data. The solid lines were calculated from least-squares third-order polynomials.

TABLE 2: Expansion Coefficients k_{nu} for the Perturbation Potential $U(Q_1)$[a]

	DME·CHF$_3$	DME·CHClF$_2$	DME·CHCl$_2$F	DME·CHCl$_3$
k_{1u}	41.3 (5)	19.5 (1)	7.1 (8)	-28.1 (1)
k_{2u}	9.7 (4)	9.5 (1)	8.2 (2)	6.1 (1)
k_{3u}	0.6 (1)	0.57 (3)	0.02 (3)	-0.04 (2)

[a] All values are given in cm^{-1}.

the C−H oscillator are influenced but weakly by the potential $U(Q_1)$ because of complexation. From this, it can be anticipated that the approximation made to transform eq 4 into eq 5 is acceptable. This was verified by calculating both the $\Delta\nu_n{}^t$ and the $\Delta\nu_n{}^a$. The former were derived from the eigenvectors calculated for H_t in a perturbation calculation using the first 20 harmonic oscillator functions, and the latter were calculated with the eigenvectors obtained from H_a as described above. In agreement with anticipations, in most cases corresponding shifts differ by less than 0.1 cm^{-1}, while in the few exceptions the differences are limited to a few percent. Thus, the quantities in eq 5 can be used to interpret the complexation shifts. The values of the shifts $\Delta\nu_n{}^a$ have been collected in Table 3. Inspection shows that $\Delta\nu_3{}^a$ is always significantly smaller than the other contributions, which means that it has little or no influence on the total complexation shift. Therefore, we will not consider this shift in the further discussion.

The sign of k_{3a} makes that for odd values of p the matrix elements $\langle a,i|Q_1{}^p|a,i \rangle$ are positive, and the more so for $i = 1$ than for $i = 0$. The same property holds for positive values of p. It follows that the expressions in square brackets in eq 5 always have positive values. Hence, the shifts $\Delta\nu_n{}^a$ have the

TABLE 3: Complexation Shifts Obtained for the Complexes of CHF_3, $CHClF_2$, $CHCl_2F$, and $CHCl_3$ with Dimethyl Ether

	DME·CHF_3	DME·$CHClF_2$	DME·$CHCl_2F$	DME·$CHCl_3$
	Direct Diagonalization of H_a and H_t			
$\nu_{monomer}$	3155.2	3136.1	3127.7	3125.4
$\nu_{complex}$	3181.8	3155.7	3140.7	3123.9
$\Delta\nu$	+26.6	+19.6	+13.0	−1.5
	Equation 5			
$\Delta\nu_1^a$	13.4	6.4	2.4	−9.4
$\Delta\nu_2^a$	12.5	12.3	10.7	8.0
$\Delta\nu_3^a$	1.0	1.0	0.0	−0.1
$\Delta\nu$	+27.0	+19.7	+13.1	−1.5
	Harmonic Force Field Calculations[a]			
$\nu_{monomer}$	3272.0	3255.8	3250.3	3249.7
$\nu_{complex}$	3289.7	3268.9	3261.0	3245.2
$\Delta\nu$	+17.7	+13.1	+10.7	−4.5
	Harmonic Frequencies Derived from Eqs 1 and 2			
$\nu_{monomer}$	3261.0	3244.8	3239.2	3238.6
$\nu_{complex}$	3283.2	3260.3	3249.6	3235.9
$\Delta\nu$	+22.2	+15.5	+10.4	−2.7
	Experiment[b]			
$\Delta\nu$	16 (1)[c]	10.6	4.8	−8.3

[a] Harmonic frequencies obtained at the MP2=FULL/6-31++G(d,p) level. [b] Taken from refs 8, 36, and 50. [c] Value obtained after correcting for the $\nu_1/2\nu_4$ Fermi resonance in monomer and complex.[50]

same sign as the corresponding k_{nu}, positive values of k_{nu} inducing blue shifts, and negative values inducing red shifts.

A positive value of k_{2u} results in a higher harmonic force constant for the C−H stretch upon formation of the complex, which amounts to a stiffening of the C−H bond. The k_{2u} term in $U(Q_1)$ does not shift the equilibrium position of the hydrogen atom with respect to the haloform carbon atom. A positive value of k_{1u} corresponds to a repulsive interaction of the Lewis base with the hydrogen atom and it is straightforward to show from eq 2 that this causes a decrease of the C−H bond length. In contrast, a negative value of k_{1u} corresponds to an attractive interaction, leading to an increase in C−H bond length.

The results in Table 2 indicate that for weakly bound complexes involving a CH···O hydrogen bond, at least two different sign combinations of k_{1u} and k_{2u} can occur. The values of k_{2u} for the present complexes are positive. Thus, the complexation with dimethyl ether induces a stiffening of the haloform C−H bond. As anticipated, this term contributes a blue shift, as is clear from Table 3. The value of k_{2u} depends only weakly on the Lewis acid, its value decreasing from 9.7(4) cm^{-1} for the fluoroform complex to 6.1(1) cm^{-1} for the chloroform complex. Evidently, the variation of $\Delta\nu_2^a$ with the Lewis acid is also low.

Table 2 shows that the value of k_{1u} varies strongly across the Lewis acids, from 41.3(5) cm^{-1} for fluoroform to −28.1(1) cm^{-1} for chloroform. The ensuing shifts $\Delta\nu_1^a$ are to the blue for fluoroform through dichlorofluoromethane, but to the red for chloroform. The total complexation shifts, also given in Table 3, are positive, that is, to the blue, for the former haloforms, while for the chloroform complex a small red shift is predicted.

It is of interest to relate the complexation shifts to the strength of the complexes. Therefore, in Figure 3 the values of $\Delta\nu_1^a$ and $\Delta\nu_2^a$ are given as function of the ab initio complexation energy. The energies were calculated at the MP2/6-311+G(d,p) level.[8] It can be seen that both shifts decrease with increasing complexation energy, and thus with increasing strength of the complex, but not to the same extent. This allows the following interpretation. For the weaker complexes, the blue shift $\Delta\nu_1^a$ induced by the stiffening of the C−H bond is enhanced by the blue shift $\Delta\nu_2^a$ due to the repulsive nature of the interaction.
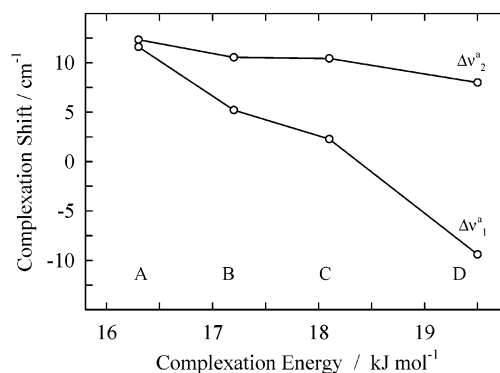

Figure 3. Complexation shifts due to the first and the second derivative of the intermolecular perturbation potential $U(Q_1)$ for the complexes DME·CHF_3 (A), DME·$CHClF_2$ (B), DME·$CHCl_2F$ (C), DME·$CHCl_3$ (D), as function of the ab initio complexation energy of the complex.

The stiffening of the C−H bond is not greatly affected by the strength of the complex, which contrasts with the repulsive nature of the interaction with the Lewis base, which rapidly weakens as the strength of the complex increases, and which has changed into an attraction for the chloroform complex. This evolution causes the blue shift to decrease rapidly with the strength of the complex and to change into a red shift for the chloroform complex.

The description of the interaction potential U as a superposition of a linear and a quadratic term is a consequence of a simple series expansion. This is both its strong and its weak point. Strong because the procedure is mathematically straightforward, but weak because it makes very difficult the interpretation of the results in terms of widely used chemical bonding concepts, such as is done in the recently proposed hyperconjugation/rehybridization model.[32] In that model, the observed shift of the C−H stretching is a balance between a red shift due to the n(O)→σ^*(CH) hyperconjugative interaction and a blue shift caused by a rehybridization of the haloform carbon atom. In terms of this model, the evolution from the fluoroform to the chloroform complex can be seen to be a change from a domination by the rehybridization contribution to a domination by the hyperconjugative contribution. It is, however, very difficult to discuss the evolution of k_{1u} and k_{2u} in terms of that model because the two models rely on different partitionings of the observed phenomena. This is easily demonstrated by the fact that the two contributions in the Alabugin model[32] have opposite effects on the C−H bond length, while it has been stressed above that the stiffening of the C−H bond, related to the k_{2u} term in the potential, has no influence on the C−H bond length. Whereas the term in k_{1u} could be interpreted in terms of the repulsion between the haloform and the hydrogen-bond acceptor, a similar straigthforward interpretation of the value of k_{2u} is not evident.

It is tempting to exploit the reasonably linear correlation of the quantities in Figure 3 to predict complexation shifts for stronger complexes. Such extrapolations must, however, be treated with care, as preliminary calculations show that the parameters of the $\Delta\nu/\Delta E$ relation are strongly dependent on the nature of the Lewis base involved in the complex. This can be illustrated with the fluoroform/trimethylamine complex, for which the complexation energy at the same level is 19.1 kJ mol^{-1}, and the predicted red shift is −58.7 cm^{-1}.[48]

Table 3 also lists the experimentally observed complexation shifts. Comparison with the values predicted with the above model learns that the latter are not completely satisfactory. The model correctly predicts the direction of the complexation shift

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for all the complexes studied, but the quantitative agreement leaves to be desired: the blue shifts are systematically overestimated, and the red shift is seriously underestimated. There may be several culprits for this. In the first place, it must be asked in how far the model used for the calculation of $U(Q_1)$ is realistic. Some insight in this can come from a comparison of the harmonic complexation shifts calculated from eq 2 with those predicted directly from ab initio calculations, which are also given in Table 3. The difference between the two is that, unlike for the calculation of $U(Q_1)$, for the ab initio calculations there is no need to keep rigid certain parts of the complex, and the haloform C−H stretching is treated as it occurs in the complex. To derive the harmonic frequency for the complex from eq 2, it is necessary to transform Q_1 into the dimensionless normal coordinate of the complex. The latter differs from Q_1 because of the shift in the position of the minimum in the vibrational potential and because of the slightly different frequency for the complex. The harmonic frequency shifts calculated in this way have also been collected in Table 3 and it can be seen that they are in acceptable agreement with the ab initio values. This suggests that there is no reason to believe that our model should do worse when the anharmonic contributions are taken into account. Therefore, the above lack of agreement must be due to other aspects of the model.

A presumably minor contribution is the reduction of the full vibrational description of the haloform to the one-dimensional approach applied here. Also of minor influence can be the fact that the shifts originating from different orders of the vibrational potential have been treated without scaling factors despite the common experience that second-order force constants tend to be less accurate than those belonging to other orders.

The most likely reason for the poor quantitative agreement of the present model, however, is the absence of averaging of the shift over the other vibrations, in particular the van der Waals modes of the complex. The complexation shift of the C−H stretch is sensitive to the orientation and distance of the Lewis base with respect to the haloform, and for a comparison of the calculated shifts with experiment it is necessary to average the former over all vibrations that affect these structural parameters.

For a nuclear configuration in which the C−H···O bond angle deviates from its equilibrium value, the interaction between the C−H bond and the Lewis base will in general be smaller than in the global minimum, and the ν_{CH} complexation shift will be reduced. Hence, averaging the calculated shifts over vibrational modes in which such conformations are generated can result in a significant reduction of the absolute value of the complexation shift. This effect has been convincingly demonstrated for the complexes of HF with Ne and Ar,[5] and the dependence of the ν_{HF} stretching frequency on relative orientations has also been demonstrated for the complexes of HF with N_2 and CO.[4] Such a reduction rationalizes the results for the blue shifting complexes, but at first sight does not do so for the chloroform complex. It is not unreasonable to assume that the averaging reduces both $\Delta\nu_1{}^a$ and $\Delta\nu_2{}^a$, but there is no reason they have to be reduced to the same extent. For the present blue shifting complexes this does not make a difference, but if the averaging reduces $\Delta\nu_1{}^a$ less than $\Delta\nu_2{}^a$ for the chloroform complex, an increased red shift results. It, therefore, may well be that the averaging also rationalizes the deviation between calculated and observed shift for the chloroform complex.

Apart from vibrational modes that affect the C−H···O angle, averaging must also be performed over the hydrogen-bond-stretching mode. This mode is quite anharmonic,[49] and thermal averaging puts the Lewis acid at a greater distance from the base than in the equilibrium geometry, and this also contributes to the reduction of the shift.

The ab initio calculations in this study have been performed using a basis set of moderate quality. Undoubtedly, more accurate frequency shifts would be obtained by using basis sets of higher quality. For the complexes studied here, constraints on computational resources presently prevent such calculations and, in view of the calculational approach used, also prevent a sufficiently sophisticated averaging over the van der Waals modes. It is, however, not overly optimistic to expect that such calculations will be possible before long.

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