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A reduced radial potential energy function for the halogen bond and the hydrogen bond in complexes B···XY and B···HX, where X and Y are halogen atoms

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It is shown by considering 76 halogen- and hydrogen-bonded complexes B···XY and B···HX (where B is a Lewis base N_2, CO, C_2H_2, C_2H_4, H_2S, HCN, H_2O, PH_3 or NH_3 and X, Y are F, Cl, Br or I) that the intermolecular stretching force constants k_σ (determined from experimental centrifugal distortion constants *via* a simple model) and the intermolecular dissociation energies D_σ (calculated at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory) are related by $D_\sigma = C_\sigma k_\sigma$, where $C_\sigma = 1.50(3) \times 10^3$ m^2 mol^{-1}. This suggests that one-dimensional functions implying direct proportionality of D_σ and k_σ, (*e.g.* a Morse or Rydberg function) might serve as reduced radial potential energy functions for such complexes.

1. Introduction

During the last decade there has been a rapid growth of interest in the halogen bond across the disciplines of Chemistry, Materials Science and Biology,[1] especially in its parallels with the hydrogen bond.[2] The halogen bond[3] is represented conventionally by the three centred dots in B···X–R, where the halogen atom X of the molecule X–R interacts with a nucleophilic acceptor atom/centre Z of a simple Lewis base B or of a much larger molecule. There has naturally followed discussion of both the radial and angular potential energy functions associated with such interactions.[4,5] This article is concerned with the characteristics of the one-dimensional function that describes the variation of the energy with the intermolecular distance r(Z···X), that is the intermolecular radial potential energy function. Attention will be focussed initially on several series of halogen-bonded complexes B···XY, where B is one of the Lewis bases N_2, CO, C_2H_2, C_2H_4, H_2S, HCN, H_2O, PH_3 and NH_3 and XY is one of the dihalogen molecules F_2, ClF, Cl_2, BrCl, Br_2 and ICl. Thereafter, the corresponding series of hydrogen-bonded complexes B···HX, where X = F, Cl, Br or I, will be discussed.

Two important characteristics of such a one-dimensional radial potential energy function are the intermolecular dissociation energy D_σ and the intermolecular quadratic stretching force constant k_σ, both of which provide a measure of the strength of the (generally weak) interaction of B and XY. D_σ is the energy required to take the complex from the equilibrium distance r_e along r to infinite separation, while k_σ is the curvature of the function at r_e and provides a measure of the restoring force per unit infinitesimal displacement from r_e along the same path.

In this article, a direct proportionality of D_σ and k_σ is established for many complexes of the halogen-bonded type B···XY and the hydrogen-bonded type B···HX. The values of D_σ were obtained by means of *ab initio* calculations at the explicitly correlated level of theory CCSD(T)(F12*)/cc-pVDZ-F12, after correction for basis set superposition error, while the k_σ values were those established from the rotational spectra of B···XY or B···HX through interpretation of experimental zero-point centrifugal distortion constants in terms of a simple model. The k_σ are therefore zero-point, rather than equilibrium, values and are also subject to errors introduced by the assumption of rigid subunits B and XY (or HX). The fact that the equation $D_\sigma = C_\sigma k_\sigma$ describes, with the same constant of proportionality C_σ, the behaviour of a large number of complexes B···XY and B···HX suggests that, for example, a reduced Morse function $V(r) = D_\sigma[1 - e^{-a(r-r_e)}]^2$, with $a = (2C_\sigma)^{-\frac{1}{2}}$, or a reduced Rydberg function $V(r) = -D_\sigma[1 + b(r - r_e)]e^{-b(r-r_e)}$, with $b = C_\sigma^{-\frac{1}{2}}$, could be useful to describe the radial intermolecular potential energy functions in such molecules.

2. Methods

2.1 k_σ values from centrifugal distortion constants

In the quadratic approximation and with the assumption of rigid subunits B and XY unperturbed by the weak interaction, Millen[6] showed that the quartic centrifugal distortion constant D_J for a linear or symmetric top complex B···XY (or B···HX) is

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simply related to the intermolecular stretching force constant by the expression

$$k_\sigma = (16\pi^2\mu B^3/D_J)[1 - B/B_B - B/B_{XY}], \quad (1)$$

in which B, B_B and B_{XY} are strictly the equilibrium rotational constants of the complex, B and XY, respectively, and $\mu = m_B m_{XY}/(m_B + m_{XY})$ is the reduced mass for the intermolecular motion in question. When B···XY is an asymmetric-top molecule of C_{2v} symmetry, in which XY lies along the C_2 axis, the corresponding centrifugal distortion constant Δ_J, obtained by fitting the rotational transitions by means of a Hamiltonian that employs the Watson A reduction in the I^r representation, is given by

$$k_\sigma = (8\pi^2\mu/\Delta_J)[B^3(1 - b) + C^3(1 - c)], \quad (2)$$

in which $b = (B/B_B) + (B/B_{XY})$ and $c = (C/B_B) + (C/B_{XY})$, and B and C are equilibrium rotational constants of the complex. When Δ_J is used, eqn (2) holds whether the C_{2v} molecule B···XY is planar, as in C_2H_2···XY, or non-planar, as in C_2H_4···XY where XY is perpendicular to the plane containing the ethene nuclei. Identical equations, with XY replaced by HX, apply to the corresponding members of the series of hydrogen-bonded complexes B···HX.

Equilibrium values of the spectroscopic constants required for use in eqn (1) and (2) to obtain k_σ have not been determined experimentally for complexes of the type considered here and in general only zero-point quantities are available. To allow progress, we invoke a type of 'effective' rigid-rotor approximation, namely the use of zero-point centrifugal distortion constants and rotational constants in these equations in place of their equilibrium counterparts. The utility of this approximation can be judged, in general, by the conclusions presented in this article and, in particular, by reference in Section 4 to the examples of the simple linear complexes OC···HX and OC···XY, for which tests of the approximation are available.

Values of k_σ calculated by means of the appropriate eqn (1) or (2) for a wide range of complexes B···XY,[7–52] where the Lewis base B is one of N_2, CO, C_2H_2, C_2H_4, H_2S, HCN, H_2O, PH_3 and NH_3 and XY is one of the dihalogen molecules F_2, ClF, Cl_2, BrCl, Br_2 and ICl are given in Tables 1 and 2, while Table 3 collects together the values of k_σ for the corresponding set of

Table 1 Some observed and calculated properties of halogen-bonded complexes B···X_2 involving non-polar dihalogen molecules X_2[a]

Lewis base B	Dihalogen molecules X_2											
	Difluorine F_2				Dichlorine Cl_2				Dibromine Br_2			
	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X$_i$)/Å	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X$_i$)/Å	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X$_i$)/Å
OC	—	—	—	—	3.68(1)	12	5.19	3.145	5.03(2)	20	7.26	3.111
C_2H_2	—	—	—	—	5.61(1)	13	7.45	3.146	7.80(3)	21	10.69	3.106
C_2H_4	—	—	—	—	5.88(2)	14	8.61	3.092	8.8(2)	22	12.93	3.004
H_2S	2.34(1)	7	3.43	3.143	6.23(2)	15	8.53	3.246	9.8(2)	23	13.68	3.131
H_3P	—	—	—	—	5.58(2)	16	8.34	3.222	9.79(3)	24	15.07	3.013
HCN	2.62(1)	8	4.15	2.811	6.55(2)	17	9.71	2.921	—	—	—	—
H_2O	3.66(1)	9 and 10	4.63	2.696	7.98(3)	18	10.66	2.808	9.9(2)	25	14.64	2.804
H_3N	4.67(1)	11	6.59	2.679	12.73(2)	19	17.85	2.681	18.5(4)	26	27.36	2.601

[a] Values of k_σ are either taken directly from the reference having the number indicated in columns 3, 7 or 11, as appropriate, or are recalculated from the centrifugal distortion constant D_J or Δ_J given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant. D_σ and r(Z···X$_i$) are equilibrium values calculated *ab initio* at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory (see text). r(Z···X$_i$) is the distance from the acceptor atom/centre Z in the Lewis base B to the inner halogen atom X$_i$.

Table 2 Some observed and calculated properties of halogen-bonded complexes B···XY involving polar dihalogen molecules XY[a]

Lewis base B	Dihalogen molecules XY											
	Chlorine monofluoride ClF				Bromine monochloride BrCl				Iodine monochloride ICl			
	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X)/Å	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X)/Å	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···X)/Å
N_2	5.00(3)	27	6.28	2.918	4.40(2)	35	5.63	3.106	5.37(2)	44	7.08	3.187
OC	7.04(2)	28	10.56	2.772	6.27(5)	36	9.20	3.006	8.00(3)	45	12.73	3.003
C_2H_2	10.01(2)	29	13.68	2.859	9.48(6)	37	12.92	3.038	12.12(8)	46	17.22	3.090
C_2H_4	11.01(3)	30	17.01	2.730	10.54(1)	38	15.74	2.927	14.0(1)	47	21.49	2.958
H_2S	13.40(3)	31	18.13	2.835	12.07(10)	39	16.65	3.057	16.55(5)	48	22.65	3.120
H_3P	—	—	—	—	11.56(7)	40	19.30	2.878	20.7(1)	49	28.88	2.898
HCN	12.33(5)	32	18.42	2.639	11.09(10)	41	16.83	2.826	14.5(1)	50	23.66	2.840
H_2O	14.24(3)	33	20.14	2.544	12.08(2)	42	18.05	2.735	15.9(2)	51	24.65	2.776
H_3N	34.3(5)	34	40.43	2.304	26.7(3)	43	34.01	2.532	30.4(3)	52	46.75	2.599

[a] Values of k_σ are either taken directly from the reference having the number indicated in columns 3, 7 or 11, as appropriate, or are recalculated from the centrifugal distortion constant D_J or Δ_J given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant. D_σ and r(Z···X) are equilibrium values calculated *ab initio* at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory (see text). r(Z···X) is the distance from the acceptor atom/centre Z in the Lewis base B to the inner halogen atom X.

Table 3 Some observed and calculated properties of hydrogen-bonded complexes B···HX[a]

Lewis base B	Hydrogen halide molecules HX							
	Hydrogen fluoride HF				Hydrogen chloride HCl			
	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···H)/Å	k_σ/(N m^{-1})	Ref.	D_σ/(kJ mol^{-1})	r(Z···H)/Å
N_2	5.13(3)	53	9.26	2.099	2.55(1)	62 and 63	5.12	2.400
OC	8.48(9)	54	14.21	2.103	3.88(1)	64	7.78	2.393
C_2H_2	—	—	—	—	6.4(3)	65	11.03	2.378
C_2H_4	—	—	—	—	5.88(16)	66	11.32	2.396
H_2S	12.0(2)	55 and 56	20.36	2.284	6.81(1)	67	12.73	2.480
H_3P	10.94(4)	57	19.38	2.354	6.01(2)	68	11.89	2.569
HCN	18.26(5)	58	30.33	1.859	9.25(4)	69	18.33	2.092
H_2O	24.51(2)	59 and 60	35.34	1.721	12.72(12)	70	21.34	1.912
H_3N	32.8	61	50.98	1.703	18.2(3)	71	32.72	1.820
	Hydrogen bromide HBr				Hydrogen iodide HI			
N_2	1.92(1)	72	3.98	2.503	—	—	—	—
OC	2.99(1)	73	6.08	2.489	1.713(1)	81	4.02	2.675
C_2H_2	5.39(2)	74	9.24	2.440	—	—	—	—
C_2H_4	5.21(2)	75	9.65	2.456	—	—	—	—
H_2S	5.86(2)	76	11.01	2.526	4.02(1)	82	7.78	2.670
H_3P	5.05(1)	77	10.19	2.618	3.409(2)	83	7.17	2.778
HCN	7.64(2)	78	14.92	2.161	4.44(1)	84	10.42	2.319
H_2O	10.06(15)	79	17.53	1.969	6.64(1)	85	12.06	2.117
H_3N	13.4(3)	80	28.60	1.800	7.18(6)	86	19.82	1.926

[a] Values of k_σ are either taken directly from the reference having the number indicated in columns 3 or 7, as appropriate, or are recalculated from the centrifugal distortion constant D_J or Δ_J given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant. D_σ and r(Z···H) are equilibrium values calculated *ab initio* at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory (see text). r(Z···H) is the distance from the acceptor atom/centre Z of the Lewis base B to the hydrogen atom H.

hydrogen-bonded complexes B···HX.[53–86] All complexes considered here, except for those involving H_2O and H_2S, are either linear molecules, symmetric-top molecules or have C_{2v} symmetry, so that eqn (1) and (2) are strictly applicable at equilibrium. All complexes of H_2O with either HX or XY are effectively planar, that is although the equilibrium geometry has a pyramidal conformation at O (C_s symmetry) there is rapid inversion in the zero-point state between the two equivalent conformers and the vibrational wavefunctions have C_{2v} symmetry. Eqn (2) is then a reasonable approximation. Complexes H_2S···HX/XY, on the other hand, all have C_s symmetry and are non-inverting in the zero-point state. They have a right-angled geometry in which HX or XY lies along an axis that passes through the H_2S centre of mass and is very nearly perpendicular to the H_2S plane. Nevertheless, eqn (2) is probably an acceptable approximation for the H_2S complexes.

2.2 Calculation of D_σ values

Values of the energy change, D_σ, accompanying the dissociation B···XY = B + XY of each of the complexes B···XY into the components B and XY, all in their (hypothetical) equilibrium electronic ground states, were calculated at the explicitly correlated level[87] CCSD(T)(F12*)/cc-pVDZ-F12 by using the *ab initio* program MOLPRO.[88] This involved geometry optimisations of B···XY, B and XY. Corrections for basis set superposition error (BSSE) were applied using the Boys–Bernardi[89] method. An advantage of using basis functions of the type cc-pVDZ-F12, that is functions optimised for use at the explicitly correlated level of theory, is that the BSSE corrections are relatively small, typically a few percent of D_σ. The basis functions for Br and I were of the type cc-pVDZ-F12-PP, where PP indicates that a pseudo-potential is used for core electrons, and were provided by J. G. Hill of the University of Sheffield prior to their public release.[90] For some complexes B···XY it was possible to conduct calculations at the CCSD(T)(F12*)/cc-pVTZ-F12 level. This increased D_σ by approximately 5% in each case. Unfortunately, for a few complexes in the series B···BrCl, B···Br_2 and B···ICl, use of the cc-pVTZ-F12 basis functions would have proved too demanding of computer time. Therefore, in view of the systematic nature of the present investigation, it was decided to employ the highest level of theory that could be applied uniformly to all complexes considered, namely the level CCSD(T)(F12*)/cc-pVDZ-F12. Values of D_σ so calculated for halogen-bonded complexes are included in Tables 1 and 2 while those calculated by the same approach for the hydrogen-bonded analogues B···HX are in Table 3. The atoms/points Z···X–Y and Z···H–X are required by symmetry to be collinear for all B···XY and B···HX except those involving H_2O and H_2S. It has been shown, however, that the deviation from collinearity will be negligible for H_2O and H_2S complexes involving both types of non-covalent interaction[31,70] and therefore collinearity was enforced for these complexes during the geometry optimisations.

3. Results

3.1 Halogen-bonded complexes B···XY

Fig. 1 shows the calculated values of D_σ plotted as the ordinate against the experimental values of k_σ along the abscissa for the series of complexes B···Cl_2 and B···Br_2 in which B is CO, C_2H_2, C_2H_4, H_2S, HCN, H_2O, PH_3 and NH_3. Also included on the same graph are B···F_2 for B = H_2S, H_2O, HCN and NH_3, which are the

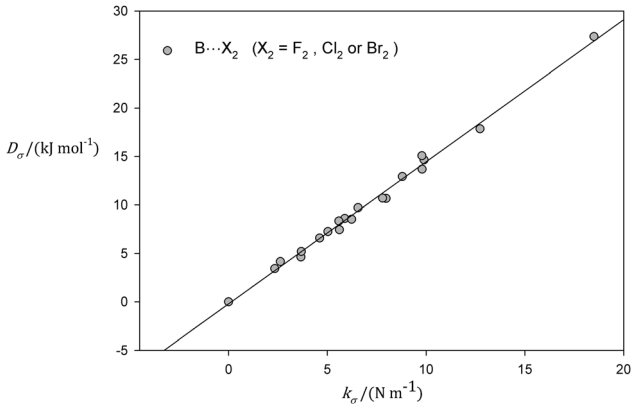

Fig. 1 A plot of D_σ *versus* k_σ for complexes of the type B···X_2, where B is one of the series of Lewis bases CO, C_2H_2, C_2H_4, H_2S, H_2O, PH_3 or NH_3 and X_2 is one of the nonpolar dihalogen molecules F_2, Cl_2 or Br_2. The continuous line represents the straight line fitted to the points (including the origin) by linear regression and is given as eqn (3) in the text.

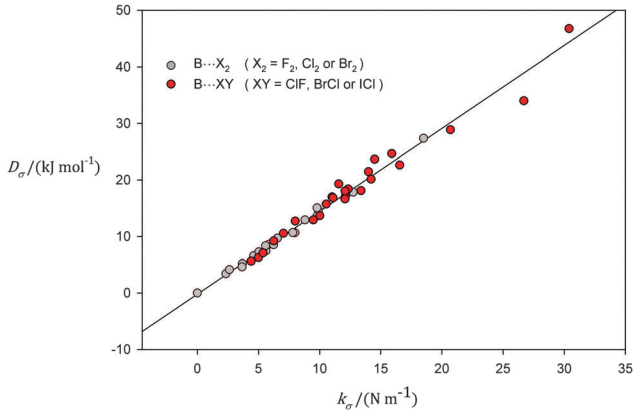

Fig. 2 A plot of D_σ against k_σ for complexes of the type B···X_2 and B···XY, where B is one of the Lewis bases N_2, CO, C_2H_2, C_2H_4, H_2S, H_2O, PH_3 or NH_3, X_2 is one of the nonpolar dihalogen molecules F_2, Cl_2 or Br_2, and XY is one of the polar dihalogens ClF, BrCl or ICl. The continuous line is that represented by eqn (3) and shown in Fig. 1, that is the straight line fitted to the points arising from B···X_2 complexes only.

only difluorine complexes known in the gas phase for the B listed and for which experimental k_σ are available. The point (0, 0) has been included under the reasonable assumption that when there is no interaction between a pair of molecules forming a complex both measures of the binding strength become zero. The points in Fig. 1 fall on a straight line through the origin, indicating direct proportionality of D_σ and k_σ. The equation for the line obtained by means of linear regression is

$$D_\sigma/(\text{kJ mol}^{-1}) = 1.47(3)\{k_\sigma/(\text{N m}^{-1})\} - 0.21(21) \quad (3)$$

The choice of B···X_2 molecules for the initial demonstration of the direct proportionality of D_σ and k_σ was dictated by the fact that in general the nonpolar molecules X_2 form weaker complexes than do their polar counterparts ClF, BrCl and ICl. Given the limitations of the model (see Section 2.1) for the experimental determination of k_σ from the centrifugal distortion constants D_J and Δ_J, especially the assumption of monomer geometries unchanged on complex formation, it is likely that the model will better apply to the B···X_2 than to those involving the polar dihalogens. Fig. 2 shows the points (k_σ, D_σ) for B···XY, when XY includes all dihalogen molecules, both polar and nonpolar. The continuous straight line in Fig. 2 corresponds to that defined in eqn (3), *i.e.* that fitted to the points for B···X_2 only. Note that the scatter from the straight line of eqn (3) tends to increase as the binding strength increases. The points with largest deviation correspond to those for complexes of H_3N with each of BrCl and ICl. For H_3N···ClF there is experimental evidence from the nuclear quadrupole coupling constants for a significant charge redistribution (and probably geometrical rearrangement) on complex formation[34] and therefore the point (k_σ, D_σ) for this complex was excluded from the graph. When all the points shown in Fig. 2 are fitted by means of linear regression, the result is

$$D_\sigma/(\text{kJ mol}^{-1}) = 1.45(3)\{k_\sigma/(\text{N m}^{-1})\} - 0.06(35), \quad (4)$$

that is, a straight line through the origin and of slope within experimental error of that obtained (eqn (3)) when only homonuclear dihalogen molecules act as the halogen-bond donor. Proportionality of k_σ and D_σ for several H_3N···XY complexes was also noted by Hill and Xu.[91]

3.2 Hydrogen-bonded complexes B···HX

It is of interest to apply the same approach to hydrogen-bonded complexes B···HX, where B is again one of the same series of simple Lewis bases N_2, CO, C_2H_2, C_2H_4, H_2S, H_2O, PH_3 and NH_3 used in the discussion of the halogen-bonded complexes in Section 3.1 and X is F, Cl, Br or I. Experimental values of k_σ obtained as before from centrifugal distortion constants and D_σ values calculated at the CCSD(T)(F12*)/cc-pVDZ level of theory are set out in Table 3. Fig. 3, in which D_σ is plotted *versus* k_σ for all members of the hydrogen-bonded series B···HX except H_3N···HBr and H_3N···HI, again reveals a reasonable straight line, with the following equation fitted by linear regression:

$$D_\sigma/(\text{kJ mol}^{-1}) = 1.53(3)\{k_\sigma/(\text{N m}^{-1})\} - 1.8(3) \quad (5)$$

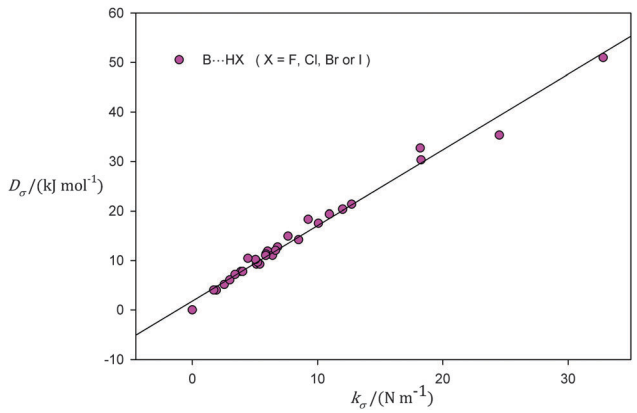

Fig. 3 A plot of D_σ against k_σ for hydrogen-bonded complexes of the type B···HX, where B is one of the Lewis bases N_2, CO, C_2H_2, C_2H_4, H_2S, H_2O, PH_3 or NH_3 and X is F, Cl, Br or I. The continuous line is that represented by eqn (5), that is the straight line fitted to the points (including the origin) by linear regression.

We note that the slope is just within experimental error of that obtained for the halogen-bonded series B···XY, but that the line does not pass as precisely through the origin. The reason for excluding $H_3N\cdots HBr$ and $H_3N\cdots HI$ is that these are the most likely to suffer from a significant contribution of $H_4N^+\cdots X^-$ to a valence bond description of the complex in view of the increased ease of dissociation $HX = H^+ + X^-$ along the series X = F, Cl, Br and I.

4. Discussion

It has been shown that it is possible to express the intermolecular dissociation energy D_σ in terms of the intermolecular stretching force constant k_σ for a wide range of simple bimolecular halogen- and hydrogen-bonded complexes B···XY and B···HX, where XY is a homo- or hetero-dihalogen molecule and X is a halogen atom, by means of the expression

$$D_\sigma = C_\sigma k_\sigma, \tag{6}$$

where the constant $C_\sigma = 1.50(3) \times 10^3\ m^2\ mol^{-1} = 2.49(5) \times 10^{-21}\ m^2$ It is not obvious why C_σ should have the same value for the hydrogen- and halogen-bonded series; it could be a coincidence. The fact that these two series of halogen- and hydrogen-bonded complexes obey eqn (6) does suggest, however, that empirical radial potential energy functions leading to a direct proportionality between k_σ and D_σ might be used to calculate the energy levels associated with the intermolecular stretching vibration in such molecules. In order to derive eqn (1) and (2) for use in the determination of k_σ, it was necessary to assume that the motion associated with k_σ involved only a change in the intermolecular distance r between the two rigid, unperturbed components while maintaining the angular geometry. Two examples of simple functions[92] that imply a relation of the type in eqn (6) are the Morse function

$$V(r) = D_\sigma[1 - e^{-a(r-r_e)}]^2, \tag{7}$$

and the Rydberg function

$$V(r) = -D_\sigma[1 + b(r - r_e)]e^{-b(r-r_e)}. \tag{8}$$

The quadratic force constant k_σ is related to $V(r)$ by $k_\sigma = \left|\frac{\partial^2 V}{\partial r^2}\right|_{r=r_e} = V''(r_e)$ so that differentiation of eqn (7) and (8) leads to the expressions $D_\sigma = k_\sigma/2a^2$ and $D_\sigma = k_\sigma/b^2$, respectively, and hence to the identifications $a = (2C_\sigma)^{-\frac{1}{2}}$ and $b = C_\sigma^{-\frac{1}{2}}$ respectively. Given values of a or b, the term values $G(v)$, as wavenumbers, for the intermolecular stretching vibration (as defined above) for any of the complexes B···XY or B···HX considered here can then be estimated by means of the usual expression

$$G(v) = \omega_\sigma(v + 1/2) - \omega_\sigma x_\sigma(v + 1/2)^2, \tag{9}$$

in which[92]

$$\omega_\sigma = (2\pi c)^{-1}[V''(r_e)/\mu]^{\frac{1}{2}} \text{ and}$$

$$\omega_\sigma x_\sigma = \left(\frac{\hbar}{\pi c \mu}\right)\left\{\frac{5}{96}\left[\frac{V'''(r_e)}{V''(r_e)}\right]^2 - \frac{1}{32}\left[\frac{V''''(r_e)}{V''(r_e)}\right]\right\}.$$

For the Morse function, ω_σ and $\omega_\sigma x_\sigma$ can then be related to the constant a in the exponential term (and thence to C_σ) by differentiation to give

$$\omega_\sigma = \frac{1}{2\pi c}\left(\frac{2a^2 D_\sigma}{\mu}\right)^{\frac{1}{2}} \text{ and } \omega_\sigma x_\sigma = \left(\frac{\hbar a^2}{4\pi c \mu}\right), \tag{10}$$

For the Rydberg function the corresponding expressions in terms of its constant b are

$$\omega_\sigma = \frac{1}{2\pi c}\left(\frac{b^2 D_\sigma}{\mu}\right)^{\frac{1}{2}} \text{ and } \omega_\sigma x_\sigma = \frac{11}{24}\left(\frac{\hbar b^2}{4\pi c \mu}\right). \tag{11}$$

The quantities ω_σ and $\omega_\sigma x_\sigma$ have proved difficult to obtain experimentally, but Bevan, Lucchese and co-workers[93–95] have determined accurate values of both for the complexes $^{16}O^{12}C\cdots H^{19}F$, $^{16}O^{12}C\cdots H^{35}Cl$, $OC\cdots{}^{35}Cl_2$ and $^{16}O^{12}C\cdots{}^{79}Br^{35}Cl$ with the aid of morphed potential energy functions for these molecules. Their values for the pairs of quantities [ω_σ and $\omega_\sigma x_\sigma$] are [107.99(2) and 3.79 cm^{-1}], [62.88(3) and 1.61 cm^{-1}], [56.43(4) and 2.91 cm^{-1}] and [58(3) and 1.87 cm^{-1}], respectively. Those calculated from the Morse function by means of eqn (10) when $C_\sigma = 1.50(3) \times 10^3\ m^2\ mol^{-1} = 2.49(5) \times 10^{-21}\ m^2$ is used are [117(2) and 2.9(1) cm^{-1}], [74.8(15) and 2.15(9) cm^{-1}], [54.2(10) and 1.69(7) cm^{-1}], and [68.0(14) and 1.51(6) cm^{-1}], respectively. The agreement between the morphed values of Bevan, Lucchese *et al.* and those generated by eqn (10) is satisfactory, but the former are more accurate. Values of $\omega_\sigma x_\sigma$ implied by the Rydberg function are smaller by the factor of 0.917 than those predicted by the Morse function.

The morphed potential energy functions for OC···HF, OC···HCl, $OC\cdots Cl_2$ and OC···BrCl reported in ref. 93–95 allow a severe test of the use of zero-point spectroscopic constants in eqn (1) and (2) in the absence of equilibrium values, as advertised in Section 2.1. The six-dimensional morphing described in ref. 93 leads to the prediction $\omega_\sigma = 107.99(2)\ cm^{-1}$ for the (experimentally unknown) equilibrium wavenumber associated with the intermolecular stretching mode σ of the isotopologue $^{16}O^{12}C\cdots H^{19}F$, which implies the value $k_\sigma = 8.017(2)\ N\ m^{-1}$ for the equilibrium quadratic force constant of that mode. By comparison, use of the centrifugal distortion constant D_J of $^{16}O^{12}C\cdots H^{19}F$ in eqn (1) in place of the unavailable equilibrium values gives $k_\sigma = 8.48(9)\ N\ m^{-1}$ (see Table 3), thereby providing some confidence in the approximations alluded to. This confidence is reinforced by the similar quality of agreement found between the values k_σ = 3.668(3), 3.751(5) and 4.5(4) implied by the ω_σ from morphed potential energy functions[94,95] of $^{16}O^{12}C\cdots H^{35}Cl$, $^{16}O^{12}C\cdots{}^{35}Cl_2$ and $^{16}O^{12}C\cdots{}^{79}Br^{35}Cl$, respectively, and those 3.88(1), 3.68(1) and 4.40(2) $N\ m^{-1}$ calculated from zero-point D_J values *via* eqn (1) (see Tables 1–3, respectively).

Finally, it has been shown[96] that k_σ values for complexes B···HX can be predicted with the aid of eqn (12)

$$k_\sigma = c' N_B E_{XY}, \quad (12)$$

where c' is a constant, from numerical nucleophilicities N_B assigned to the Lewis bases B and numerical electrophilicities E_{HX} assigned to the acids HX. A similar expression[97] holds when the Lewis acids are dihalogen molecules. In view of the direct proportionality $D_\sigma = C_\sigma k_\sigma$ established here, it follows that it is also possible to use D_σ values in a similar manner to establish nucleophilicities for Lewis bases B and electrophilicities for Lewis acids HX or XY.

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