

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

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It is shown by considering 76 halogen- and hydrogen-bonded complexes  $B \cdots XY$  and  $B \cdots HX$  (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  $k_\sigma$  (determined from experimental centrifugal distortion constants via a simple model) and the intermolecular dissociation energies  $D_\sigma$  (calculated at the CCSD(T)(F12\*)/cc-pVDZ-F12 level of theory) are related by  $D_\sigma = C_\sigma k_\sigma$ , where  $C_\sigma = 1.50(3) \times 10^3 \text{ m}^2 \text{ mol}^{-1}$ . This suggests that one-dimensional functions implying direct proportionality of  $D_\sigma$  and  $k_\sigma$ , (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,<sup>1</sup> especially in its parallels with the hydrogen bond.<sup>2</sup> The halogen bond<sup>3</sup> is represented conventionally by the three centred dots in  $B \cdots X-R$ , 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.<sup>4,5</sup> This article is concerned with the characteristics of the one-dimensional function that describes the variation of the energy with the intermolecular distance  $r(Z \cdots X)$ , that is the intermolecular radial potential energy function. Attention will be focussed initially on several series of halogen-bonded complexes  $B \cdots XY$ , 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  $B \cdots HX$ , 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  $D_\sigma$  and the intermolecular quadratic stretching force constant  $k_\sigma$ , both of which provide a measure of the strength of the (generally weak) interaction of B and XY.  $D_\sigma$  is the energy required to take the complex from the equilibrium distance  $r_e$  along  $r$  to infinite separation, while  $k_\sigma$  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  $D_\sigma$  and  $k_\sigma$  is established for many complexes of the halogen-bonded type  $B \cdots XY$  and the hydrogen-bonded type  $B \cdots HX$ . The values of  $D_\sigma$  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  $k_\sigma$  values were those established from the rotational spectra of  $B \cdots XY$  or  $B \cdots HX$  through interpretation of experimental zero-point centrifugal distortion constants in terms of a simple model. The  $k_\sigma$  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  $C_\sigma$ , the behaviour of a large number of complexes  $B \cdots XY$  and  $B \cdots HX$  suggests that, for example, a reduced Morse function  $V(r) = D_\sigma[1 - e^{-a(r-r_e)}]^2$ , with  $a = (2C_\sigma)^{-1/2}$ , or a reduced Rydberg function  $V(r) = -D_\sigma[1 + b(r-r_e)]e^{-b(r-r_e)}$ , with  $b = C_\sigma^{-1/2}$ , could be useful to describe the radial intermolecular potential energy functions in such molecules.

## 2. Methods

### 2.1 $k_\sigma$ 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<sup>6</sup> showed that the quartic centrifugal distortion constant  $D_J$  for a linear or symmetric top complex  $B \cdots XY$  (or  $B \cdots HX$ ) 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  $B \cdots XY$  is an asymmetric-top molecule of  $C_{2v}$  symmetry, in which  $XY$  lies along the  $C_2$  axis, the corresponding centrifugal distortion constant  $\Delta_J$ , obtained by fitting the rotational transitions by means of a Hamiltonian that employs the Watson A reduction in the  $I'$  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  $\Delta_J$  is used, eqn (2) holds whether the  $C_{2v}$  molecule  $B \cdots XY$  is planar, as in  $C_2H_2 \cdots XY$ , or non-planar, as in  $C_2H_4 \cdots XY$  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  $B \cdots HX$ .

Equilibrium values of the spectroscopic constants required for use in eqn (1) and (2) to obtain  $k_{\sigma}$  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  $OC \cdots HX$  and  $OC \cdots XY$ , for which tests of the approximation are available.

Values of  $k_{\sigma}$  calculated by means of the appropriate eqn (1) or (2) for a wide range of complexes  $B \cdots XY$ ,<sup>7–52</sup> 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  $k_{\sigma}$  for the corresponding set of

**Table 1** Some observed and calculated properties of halogen-bonded complexes  $B \cdots X_2$  involving non-polar dihalogen molecules  $X_2$ <sup>a</sup>

Lewis base B	Dihalogen molecules $X_2$											
	Difluorine $F_2$				Dichlorine $Cl_2$				Dibromine $Br_2$			
	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X_i)/\text{\AA}$	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X_i)/\text{\AA}$	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X_i)/\text{\AA}$
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

<sup>a</sup> Values of  $k_{\sigma}$  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  $\Delta_J$  given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant.  $D_{\sigma}$  and  $r(Z \cdots X_i)$  are equilibrium values calculated *ab initio* at the CCSD(T)(F12\*)/cc-pVDZ-F12 level of theory (see text).  $r(Z \cdots X_i)$  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  $B \cdots XY$  involving polar dihalogen molecules  $XY$ <sup>a</sup>

Lewis base B	Dihalogen molecules $XY$											
	Chlorine monofluoride $ClF$				Bromine monochloride $BrCl$				Iodine monochloride $ICl$			
	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X)/\text{\AA}$	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X)/\text{\AA}$	$k_{\sigma}/(N m^{-1})$	Ref.	$D_{\sigma}/(kJ mol^{-1})$	$r(Z \cdots X)/\text{\AA}$
$N_2$	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

<sup>a</sup> Values of  $k_{\sigma}$  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  $\Delta_J$  given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant.  $D_{\sigma}$  and  $r(Z \cdots X)$  are equilibrium values calculated *ab initio* at the CCSD(T)(F12\*)/cc-pVDZ-F12 level of theory (see text).  $r(Z \cdots X)$  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  $B \cdots HX^a$ 

Lewis base B	Hydrogen halide molecules HX							
	Hydrogen fluoride HF				Hydrogen chloride HCl			
	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$
N <sub>2</sub>	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 <sub>2</sub> H <sub>2</sub>	—	—	—	—	6.4(3)	65	11.03	2.378
C <sub>2</sub> H <sub>4</sub>	—	—	—	—	5.88(16)	66	11.32	2.396
H <sub>2</sub> S	12.0(2)	55 and 56	20.36	2.284	6.81(1)	67	12.73	2.480
H <sub>3</sub> P	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 <sub>2</sub> O	24.51(2)	59 and 60	35.34	1.721	12.72(12)	70	21.34	1.912
H <sub>3</sub> N	32.8	61	50.98	1.703	18.2(3)	71	32.72	1.820
Lewis base B	Hydrogen bromide HBr				Hydrogen iodide HI			
	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$
	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$	$k_\sigma/(N\ m^{-1})$	Ref.	$D_\sigma/(kJ\ mol^{-1})$	$r(Z \cdots H)/\text{\AA}$
N <sub>2</sub>	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 <sub>2</sub> H <sub>2</sub>	5.39(2)	74	9.24	2.440	—	—	—	—
C <sub>2</sub> H <sub>4</sub>	5.21(2)	75	9.65	2.456	—	—	—	—
H <sub>2</sub> S	5.86(2)	76	11.01	2.526	4.02(1)	82	7.78	2.670
H <sub>3</sub> P	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 <sub>2</sub> O	10.06(15)	79	17.53	1.969	6.64(1)	85	12.06	2.117
H <sub>3</sub> N	13.4(3)	80	28.60	1.800	7.18(6)	86	19.82	1.926

<sup>a</sup> Values of  $k_\sigma$  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  $D_f$  or  $A_f$  given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant.  $D_\sigma$  and  $r(Z \cdots H)$  are equilibrium values calculated *ab initio* at the CCSD(T)(F12\*)/cc-pVDZ-F12 level of theory (see text).  $r(Z \cdots H)$  is the distance from the acceptor atom/centre Z of the Lewis base B to the hydrogen atom H.

hydrogen-bonded complexes  $B \cdots HX$ .<sup>53–86</sup> All complexes considered here, except for those involving H<sub>2</sub>O and H<sub>2</sub>S, 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<sub>2</sub>O 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<sub>2</sub>S  $\cdots$  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<sub>2</sub>S centre of mass and is very nearly perpendicular to the H<sub>2</sub>S plane. Nevertheless, eqn (2) is probably an acceptable approximation for the H<sub>2</sub>S complexes.

## 2.2 Calculation of $D_\sigma$ values

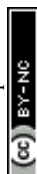
Values of the energy change,  $D_\sigma$ , accompanying the dissociation  $B \cdots XY = B + XY$  of each of the complexes  $B \cdots XY$  into the components B and XY, all in their (hypothetical) equilibrium electronic ground states, were calculated at the explicitly correlated level<sup>87</sup> CCSD(T)(F12\*)/cc-pVDZ-F12 by using the *ab initio* program MOLPRO.<sup>88</sup> This involved geometry optimisations of  $B \cdots XY$ , B and XY. Corrections for basis set superposition error (BSSE) were applied using the Boys–Bernardi<sup>89</sup> 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  $D_\sigma$ . 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.<sup>90</sup> For some complexes  $B \cdots XY$  it was possible to conduct calculations at the CCSD(T)(F12\*)/cc-pVTZ-F12 level. This increased  $D_\sigma$  by approximately 5% in each case. Unfortunately, for a few complexes in the series  $B \cdots BrCl$ ,  $B \cdots Br_2$  and  $B \cdots ICl$ , 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  $D_\sigma$  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  $B \cdots HX$  are in Table 3. The atoms/points  $Z \cdots X-Y$  and  $Z \cdots H-X$  are required by symmetry to be collinear for all  $B \cdots XY$  and  $B \cdots HX$  except those involving H<sub>2</sub>O and H<sub>2</sub>S. It has been shown, however, that the deviation from collinearity will be negligible for H<sub>2</sub>O and H<sub>2</sub>S complexes involving both types of non-covalent interaction<sup>31,70</sup> and therefore collinearity was enforced for these complexes during the geometry optimisations.

## 3. Results

### 3.1 Halogen-bonded complexes $B \cdots XY$

Fig. 1 shows the calculated values of  $D_\sigma$  plotted as the ordinate against the experimental values of  $k_\sigma$  along the abscissa for the series of complexes  $B \cdots Cl_2$  and  $B \cdots Br_2$  in which B is CO, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>S, HCN, H<sub>2</sub>O, PH<sub>3</sub> and NH<sub>3</sub>. Also included on the same graph are  $B \cdots F_2$  for B = H<sub>2</sub>S, H<sub>2</sub>O, HCN and NH<sub>3</sub>, which are the



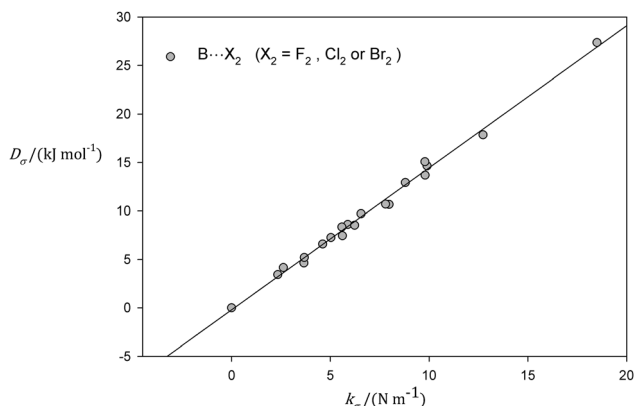


Fig. 1 A plot of  $D_\sigma$  versus  $k_\sigma$  for complexes of the type  $B \cdots X_2$ , where B is one of the series of Lewis bases CO,  $C_2H_2$ ,  $C_2H_4$ ,  $H_2S$ ,  $H_2O$ ,  $PH_3$  or  $NH_3$  and  $X_2$  is one of the nonpolar dihalogen molecules  $F_2$ ,  $Cl_2$  or  $Br_2$ . The continuous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

only difluorine complexes known in the gas phase for the B listed and for which experimental  $k_\sigma$  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  $D_\sigma$  and  $k_\sigma$ . 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  $B \cdots X_2$  molecules for the initial demonstration of the direct proportionality of  $D_\sigma$  and  $k_\sigma$  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  $k_\sigma$  from the centrifugal distortion constants  $D_J$  and  $A_J$ , especially the assumption of monomer geometries unchanged on complex formation, it is likely that the model will better apply to the  $B \cdots X_2$  than to those involving the polar dihalogens. Fig. 2 shows the points ( $k_\sigma$ ,  $D_\sigma$ ) for  $B \cdots XY$ , 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  $B \cdots X_2$  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  $H_3N \cdots ClF$  there is experimental evidence from the nuclear quadrupole coupling constants for a significant charge redistribution (and probably geometrical rearrangement) on complex formation<sup>34</sup> and therefore the point ( $k_\sigma$ ,  $D_\sigma$ ) 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.

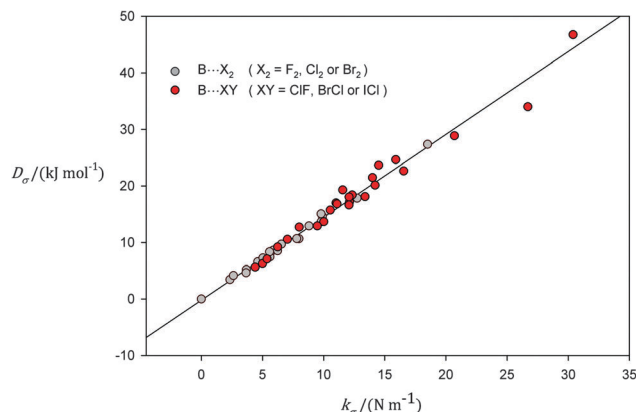


Fig. 2 A plot of  $D_\sigma$  against  $k_\sigma$  for complexes of the type  $B \cdots X_2$  and  $B \cdots XY$ , where B is one of the Lewis bases  $N_2$ , CO,  $C_2H_2$ ,  $C_2H_4$ ,  $H_2S$ ,  $H_2O$ ,  $PH_3$  or  $NH_3$ ,  $X_2$  is one of the nonpolar dihalogen molecules  $F_2$ ,  $Cl_2$  or  $Br_2$ , 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  $B \cdots X_2$  complexes only.

Proportionality of  $k_\sigma$  and  $D_\sigma$  for several  $H_3N \cdots XY$  complexes was also noted by Hill and Xu.<sup>91</sup>

### 3.2 Hydrogen-bonded complexes $B \cdots HX$

It is of interest to apply the same approach to hydrogen-bonded complexes  $B \cdots HX$ , 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  $k_\sigma$  obtained as before from centrifugal distortion constants and  $D_\sigma$  values calculated at the CCSD(T)(F12\*)/cc-pVDZ level of theory are set out in Table 3. Fig. 3, in which  $D_\sigma$  is plotted versus  $k_\sigma$  for all members of the hydrogen-bonded series  $B \cdots HX$  except  $H_3N \cdots HBr$  and  $H_3N \cdots HI$ , again reveals a reasonable straight line, with the following equation fitted by linear regression:

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

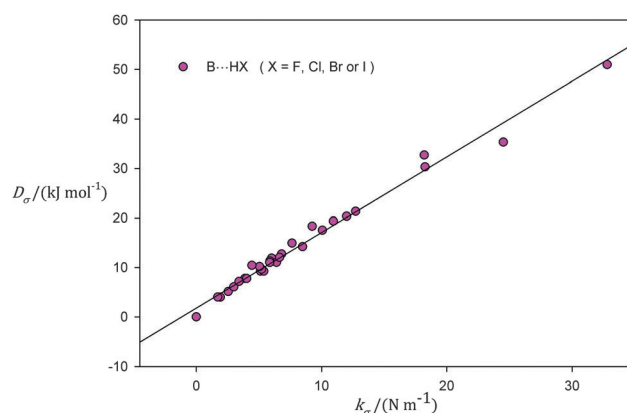


Fig. 3 A plot of  $D_\sigma$  against  $k_\sigma$  for hydrogen-bonded complexes of the type  $B \cdots HX$ , where B is one of the Lewis bases  $N_2$ , CO,  $C_2H_2$ ,  $C_2H_4$ ,  $H_2S$ ,  $H_2O$ ,  $PH_3$  or  $NH_3$  and X is F, Cl, Br or I. The continuous line is that represented by eqn (5), that 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  $B \cdots XY$ , 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  $D_\sigma$  in terms of the intermolecular stretching force constant  $k_\sigma$  for a wide range of simple bimolecular halogen- and hydrogen-bonded complexes  $B \cdots XY$  and  $B \cdots HX$ , where  $XY$  is a homo- or hetero-dihalogen molecule and  $X$  is a halogen atom, by means of the expression

$$D_\sigma = C_\sigma k_\sigma, \quad (6)$$

where the constant  $C_\sigma = 1.50(3) \times 10^3 \text{ m}^2 \text{ mol}^{-1} = 2.49(5) \times 10^{-21} \text{ m}^2$ . It is not obvious why  $C_\sigma$  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  $k_\sigma$  and  $D_\sigma$  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  $k_\sigma$ , it was necessary to assume that the motion associated with  $k_\sigma$  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<sup>92</sup> that imply a relation of the type in eqn (6) are the Morse function

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

and the Rydberg function

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

The quadratic force constant  $k_\sigma$  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  $B \cdots XY$  or  $B \cdots HX$  considered here can then be estimated by means of the usual expression

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

in which<sup>92</sup>

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

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

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

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

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

The quantities  $\omega_\sigma$  and  $\omega_\sigma x_\sigma$  have proved difficult to obtain experimentally, but Bevan, Lucchese and co-workers<sup>93–95</sup> have determined accurate values of both for the complexes  $^{16}\text{O}^{12}\text{C} \cdots \text{H}^{19}\text{F}$ ,  $^{16}\text{O}^{12}\text{C} \cdots \text{H}^{35}\text{Cl}$ ,  $\text{OC} \cdots ^{35}\text{Cl}_2$  and  $^{16}\text{O}^{12}\text{C} \cdots ^{79}\text{Br}^{35}\text{Cl}$  with the aid of morphed potential energy functions for these molecules. Their values for the pairs of quantities  $[\omega_\sigma \text{ and } \omega_\sigma x_\sigma]$  are  $[107.99(2) \text{ and } 3.79 \text{ cm}^{-1}]$ ,  $[62.88(3) \text{ and } 1.61 \text{ cm}^{-1}]$ ,  $[56.43(4) \text{ and } 2.91 \text{ cm}^{-1}]$  and  $[58(3) \text{ and } 1.87 \text{ cm}^{-1}]$ , respectively. Those calculated from the Morse function by means of eqn (10) when  $C_\sigma = 1.50(3) \times 10^3 \text{ m}^2 \text{ mol}^{-1} = 2.49(5) \times 10^{-21} \text{ m}^2$  is used are  $[117(2) \text{ and } 2.9(1) \text{ cm}^{-1}]$ ,  $[74.8(15) \text{ and } 2.15(9) \text{ cm}^{-1}]$ ,  $[54.2(10) \text{ and } 1.69(7) \text{ cm}^{-1}]$ , and  $[68.0(14) \text{ and } 1.51(6) \text{ cm}^{-1}]$ , 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  $\text{OC} \cdots \text{HF}$ ,  $\text{OC} \cdots \text{HCl}$ ,  $\text{OC} \cdots \text{Cl}_2$  and  $\text{OC} \cdots \text{BrCl}$  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  $\omega_\sigma = 107.99(2) \text{ cm}^{-1}$  for the (experimentally unknown) equilibrium wavenumber associated with the intermolecular stretching mode  $\sigma$  of the isotopologue  $^{16}\text{O}^{12}\text{C} \cdots \text{H}^{19}\text{F}$ , which implies the value  $k_\sigma = 8.017(2) \text{ N m}^{-1}$  for the equilibrium quadratic force constant of that mode. By comparison, use of the centrifugal distortion constant  $D_J$  of  $^{16}\text{O}^{12}\text{C} \cdots \text{H}^{19}\text{F}$  in eqn (1) in place of the unavailable equilibrium values gives  $k_\sigma = 8.48(9) \text{ N m}^{-1}$  (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  $k_\sigma = 3.668(3)$ ,  $3.751(5)$  and  $4.5(4)$  implied by the  $\omega_\sigma$  from morphed potential energy functions<sup>94,95</sup> of  $^{16}\text{O}^{12}\text{C} \cdots \text{H}^{35}\text{Cl}$ ,  $^{16}\text{O}^{12}\text{C} \cdots ^{35}\text{Cl}_2$  and  $^{16}\text{O}^{12}\text{C} \cdots ^{79}\text{Br}^{35}\text{Cl}$ , respectively, and those  $3.88(1)$ ,  $3.68(1)$  and  $4.40(2) \text{ N m}^{-1}$  calculated from zero-point  $D_J$  values *via* eqn (1) (see Tables 1–3, respectively).



Finally, it has been shown<sup>96</sup> that  $k_{\sigma}$  values for complexes  $B \cdots HX$  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<sup>97</sup> 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  $D_{\sigma}$  values in a similar manner to establish nucleophilicities for Lewis bases B and electrophilicities for Lewis acids HX or XY.

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