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

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

2. Methods

2.1 $k_\alpha$ 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 showed that the quartic centrifugal distortion constant $D_\gamma$ for a linear or symmetric top complex $B \cdot \cdot \cdot XY$ (or $B \cdot \cdot \cdot HX$) is
simply related to the intermolecular stretching force constant by the expression

\[
k_\sigma = (16\pi^2 \mu B^2 / D_J) [1 - B(B_n - B/B_X Y)],
\]

in which \(B\), \(B_n\) and \(B_X Y\) 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 \(C_2m\) symmetry, in which \(XY\) lies along the \(C_2\) axis, the corresponding centrifugal distortion constant \(\delta_1\) obtained by fitting the rotational transitions by means of a Hamiltonian that employs the Watson \(A\) reduction in the \(I^1\) representation, is given by

\[
k_\sigma = (8\pi^2 \mu / \delta_1) [B^2(1 - b) + C^2(1 - c)],
\]

in which \(b = [B(B_n) + B/B_X Y] / C_0\) and \(c = (C/B_n) + (C/B_X Y)\), and \(B\) and \(C\) are equilibrium rotational constants of the complex. When \(\delta_1\) is used, eqn (2) holds whether the \(C_2m\) molecule \(B \cdots XY\) is planar, as in \(\text{CH}_2\cdots \text{XY}\), or non-planar, as in \(\text{CH}_2\cdots \text{XY}\) 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 \(B \cdots XY\),\(^{-52}\) where the Lewis base \(B\) is one of \(\text{N}_2\), \(\text{CO}\), \(\text{C}_2\text{H}_2\), \(\text{C}_2\text{H}_4\), \(\text{H}_2\text{S}\), \(\text{H}_2\text{O}\), \(\text{PH}_3\) and \(\text{NH}_3\) and \(XY\) is one of the dihalogen molecules \(\text{F}_2\), \(\text{ClF}\), \(\text{Cl}_2\), \(\text{BrCl}\), \(\text{Br}_2\) and \(\text{ICl}\) 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 \(B \cdots XY\) involving non-polar dihalogen molecules \(X_Y\)^a |
|-----------------|-----------------|-----------------|-----------------|
| Lewis base \(B\) | Difluorine \(F_2\) | Dichlorine \(Cl_2\) | Dibromine \(Br_2\) |
| \(k_\sigma\) (N m\(^{-1}\)) | \(D_\sigma\) (kJ mol\(^{-1}\)) | \(r(Z \cdots X)/\AA\) | \(k_\sigma\) (N m\(^{-1}\)) | \(D_\sigma\) (kJ mol\(^{-1}\)) | \(r(Z \cdots X)/\AA\) |
| OC | — — — — | 3.68(1) | 12 | 5.19 | 3.145 | 5.03(2) | 20 | 7.26 | 3.111 |
| \(\text{C}_2\text{H}_2\) | — — — — | 5.61(1) | 13 | 7.45 | 3.146 | 7.80(3) | 21 | 10.69 | 3.106 |
| \(\text{C}_2\text{H}_4\) | — — — — | 5.88(2) | 14 | 8.61 | 3.092 | 8.8(2) | 22 | 12.93 | 3.004 |
| \(\text{H}_2\text{S}\) | 2.34(1) | 3.43 | 13 | 7.14 | 3.147 | 2.346 | 9.8(2) | 23 | 13.68 | 3.131 |
| \(\text{HCN}\) | 12.33(5) | 32 | 18.42 | 11.09(2) | 41 | 18.05 | 2.735 | 15.9(2) | 51 | 24.65 | 2.776 |

\(^a\) 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 \(D_\sigma\) or \(\delta_1\) given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant \(D_\sigma\) or \(r(Z \cdots X)/\AA\) are equilibrium values calculated ab initio at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory (see text). The \(r(Z \cdots X)/\AA\) is the distance from the acceptor atom/centre \(Z\) in the Lewis base \(B\) to the inner halogen atom \(X_Y\).

| Table 2 | Some observed and calculated properties of halogen-bonded complexes \(B \cdots XY\) involving polar dihalogen molecules XY^a |
|-----------------|-----------------|-----------------|-----------------|
| Lewis base \(B\) | Chlorine monofluoride \(\text{ClF}\) | Bromine monochloride \(\text{BrCl}\) | Iodine monochloride \(\text{ICl}\) |
| \(k_\sigma\) (N m\(^{-1}\)) | \(D_\sigma\) (kJ mol\(^{-1}\)) | \(r(Z \cdots X)/\AA\) | \(k_\sigma\) (N m\(^{-1}\)) | \(D_\sigma\) (kJ mol\(^{-1}\)) | \(r(Z \cdots X)/\AA\) | \(k_\sigma\) (N m\(^{-1}\)) | \(D_\sigma\) (kJ mol\(^{-1}\)) | \(r(Z \cdots X)/\AA\) |
| \(N_2\) | 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 |
| \(\text{C}_2\text{H}_2\) | 10.01(2) | 29 | 13.68 | 2.859 | 9.48(6) | 37 | 12.92 | 3.038 | 12.12(8) | 46 | 17.22 | 3.090 |
| \(\text{C}_2\text{H}_4\) | 11.01(3) | 30 | 17.01 | 2.730 | 10.54(1) | 38 | 15.74 | 2.927 | 14.0(1) | 47 | 21.49 | 2.958 |
| \(\text{H}_2\text{S}\) | 13.40(3) | 31 | 18.13 | 2.835 | 12.07(10) | 39 | 16.65 | 3.057 | 16.53(5) | 48 | 22.65 | 3.120 |
| \(\text{HCN}\) | 12.33(5) | 32 | 18.42 | 2.639 | 11.09(10) | 41 | 16.83 | 2.826 | 14.5(1) | 50 | 23.66 | 2.840 |
| \(\text{H}_2\text{O}\) | 14.24(3) | 33 | 20.14 | 2.544 | 12.08(2) | 42 | 18.05 | 2.735 | 15.9(2) | 51 | 24.65 | 2.776 |
| \(\text{H}_2\text{N}\) | 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 \(k_\sigma\) 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 \(D_\sigma\) or \(\delta_1\) given therein by using eqn (1) or (2). The quoted error is that transmitted by the error in the distortion constant \(D_\sigma\) or \(r(Z \cdots X)/\AA\) are equilibrium values calculated ab initio at the CCSD(T)(F12*)/cc-pVDZ-F12 level of theory (see text). The \(r(Z \cdots X)/\AA\) is the distance from the acceptor atom/centre \(Z\) in the Lewis base \(B\) to the inner halogen atom \(X_Y\).
hydrogen-bonded complexes B···HX.\(^{53-66}\) All complexes considered here, except for those involving H\(_2\)O and H\(_2\)S, are either linear molecules, symmetric-top molecules or have \(C_2\)v symmetry, so that eqn (1) and (2) are strictly applicable at equilibrium. All complexes of H\(_2\)O with either HX or XY are effectively planar, that is although the equilibrium geometry has a pyramidal conformation at O (\(C_2\) symmetry) there is rapid inversion in the zero-point state between the two equivalent conformers and the vibrational functions have \(C_2\)v symmetry. Eqn (2) is then a reasonable approximation. Complexes H\(_2\)S···HXXY, on the other hand, all have \(C_2\)v 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\(_2\)S centre of mass and is very nearly perpendicular to the H\(_2\)S plane. Nevertheless, eqn (2) is probably an acceptable approximation for the H\(_2\)S complexes.

### 2.2 Calculation of \(D_\sigma\) values

Values of the energy change, \(D_\sigma\), accompanying the dissociation B···XY \(\rightarrow\) 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\(^{67}\) CCSD(T)(F12\(^*\))/cc-pVDZ-F12 by using the \(ab\ initio\) program MOLPRO.\(^{68}\) This involved geometry optimisations of B···XY, B and XY. Corrections for basis set superposition error (BSSE) were applied using the Boys–Bernardi\(^{69}\) 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.\(^{90}\) For some complexes B···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···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 \(D_\sigma\) 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···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\(_2\)O and H\(_2\)S. It has been shown, however, that the deviation from collinearity will be negligible for H\(_2\)O and H\(_2\)S complexes involving both types of non-covalent interaction\(^{53,57}\) 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 \(D_\sigma\) plotted as the ordinate against the experimental values of \(k_\sigma\) along the abscissa for the series of complexes B···Cl\(_2\) and B···Br\(_2\) in which B is CO, C\(_2\)H\(_4\), C\(_3\)H\(_4\), H\(_2\)S, H\(_2\)O, PH\(_3\) and NH\(_3\). Also included on the same graph are B···F\(_2\) for B = H\(_2\)S, H\(_2\)O, HCN and NH\(_3\), which are the
only difluorine complexes known in the gas phase for the B
listed and for which experimental \( k_\sigma \) are available that 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 \( D_\alpha \) and \( k_\sigma \).
The equation for the line obtained by means of linear regression is

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

The choice of B–X2 molecules for the initial demonstration of the direct proportionality of \( D_\alpha \) and \( k_\sigma \) was dictated by the fact that in general the nonpolar molecules X2 form weaker complexes than
do their polar counterparts ClF, BrCl and ICl. Given the limitations
of monomer geometries unchanged on complex formation, it is likely that the model will better apply to the B–X2 than to those involving the polar dihalogens. Fig. 2 shows the points
\((k_\sigma, D_\alpha)\) for B–XY, when XY includes all dihalogen molecules, both
polar and nonpolar. The continuous straight line in Fig. 2 corre-
responds to that defined in eqn (3), i.e. that fitted to the points for
B–X2 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 H2N with
each of BrCl and ICl. For H2N–ClF there is experimental evidence
from the nuclear quadrupole coupling constants for a significant
charge redistribution (and probably geometrical rearrangement)
on complex formation14 and therefore the point \((k_\sigma, D_\alpha)\) 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

\[
D_\alpha/(kJ mol^{-1}) = 1.45(3)\{k_\sigma/(N m^{-1})\} - 0.06(35) \quad (4)
\]

that is, a straight line through the origin and of slope within
experimental error of that obtained (eqn (3)) when only homo-
nuclear dihalogen molecules act as the halogen-bond donor.

Proportionality of \( k_\sigma \) and \( D_\alpha \) for several H3N–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 N2, CO, C2H2, C2H4, H2S, H2O, PH3 or NH3
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 \( D_\alpha \)
values calculated at the CCSD(T)(F12*)/cc-pVDZ level of theory
are set out in Table 3. Fig. 3, in which \( D_\alpha \) is plotted versus \( k_\sigma \)
for all members of the hydrogen-bonded series B–HX except
H3N–HBr and H3N–HI, again reveals a reasonable straight
line, with the following equation fitted by linear regression:

\[
D_\alpha/(kJ mol^{-1}) = 1.53(3)\{k_\sigma/(N m^{-1})\} - 1.8(3) \quad (5)
\]
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 H₃N···HBr and H₃N···HI is that these are the most likely to suffer from a significant contribution of H₃N···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·XY and B·HX, where XY is a homo- or hetero-dihalogen molecule and X is a halogen atom, by means of the expression

$$D_\sigma = C_\sigma k_\sigma,$$

where the constant $C_\sigma = 1.50(3) \times 10^5 \text{ m}^2 \text{ mol}^{-1} = 2.49(5) \times 10^{-21} \text{ m}^2$. 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 that imply a relation of the type in eqn (6) are the Morse function

$$V(r) = D_\sigma \{ 1 - e^{-a(r-r_0)} \}^2,$$

and the Rydberg function

$$V(r) = -D_\sigma \{ 1 + b(r-r_0) \} e^{-b(r-r_0)}.$$  

The quadratic force constant $k_\sigma$ is related to $V(r)$ by $k_\sigma = \left( \frac{\partial^2 V}{\partial r^2} \right)_{r=r_0}$ so that differentiation of eqn (7) and (8) leads to the expressions $D_\sigma = k_\sigma/2a^2$ and $D_\sigma = k_\sigma/2b^2$, 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

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

in which

$$\omega_\sigma = (2\pi)^{-1} \left[ V''(r_0)/\mu \right]^\frac{1}{2}$$

and

$$\omega_\sigma \chi_\sigma = \left( \frac{\hbar}{\pi c \mu} \right) \left\{ \frac{5}{96} \left[ V''(r_0) \right]^2 - \frac{1}{32} \left[ V''(r_0) \right] \right\}.$$  

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

$$\omega_\sigma = \frac{1}{2\pi c} \left( \frac{2a^2 D_\sigma}{\mu} \right)^{\frac{1}{2}}$$

and $\omega_\sigma \chi_\sigma = \frac{\hbar a^2}{4\pi c \mu}$.  

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

$$\omega_\sigma = \frac{1}{2\pi c} \left( \frac{b^2 D_\sigma}{\mu} \right)^{\frac{1}{2}}$$

and $\omega_\sigma \chi_\sigma = \frac{\hbar b^2}{24 \pi c \mu}$.  

The quantities $\omega_\sigma$ and $\omega_\sigma \chi_\sigma$ have proved difficult to obtain experimentally, but Bevan, Lucchese and co-workers have determined accurate values of both for the complexes $^{16}O^{12}C$···$^{19}F$, $^{16}O^{12}C$···$^{35}Cl$, OC···Cl₂ and $^{16}O^{12}C$···$^{79}Br$Cl with the aid of morphed potential energy functions for these molecules. Their values for the pairs of quantities $[\omega_\sigma$ and $\omega_\sigma \chi_\sigma]$ 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 $[58.3(3) \text{ and } 1.87 \text{ cm}^{-1}]$, respectively. Those calculated from the Morse function by means of eqn (10) when $C_\sigma = 1.50(3) \times 10^5 \text{ m}^2 \text{ mol}^{-1} = 2.49(5) \times 10^{-21} \text{ m}^2$ is used are $[117(2) \text{ and } 2.91(1) \text{ cm}^{-1}]$, $[74.8(15) \text{ and } 2.15(9) \text{ cm}^{-1}]$, $[54.2(10) \text{ and } 1.69(7) \text{ cm}^{-1}]$, 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 $\omega_\sigma \chi_\sigma$ 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···Cl₂ 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 $\omega_\sigma = 107.99(2) \text{ cm}^{-1}$ for the (experimentally unknown) equilibrium wavenumber associated with the intermolecular stretching mode $\sigma$ of the isotopologue $^{16}O^{12}C$···$^{19}F$, 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 $D_\ell$ of $^{16}O^{12}C$···$^{19}F$ 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 of $^{16}O^{12}C$···$^{35}Cl$, $^{16}O^{12}C$···$^{79}Br$Cl, respectively, and those $3.88(1)$, $3.68(1)$ and $4.40(2) \text{ N m}^{-1}$ calculated from zero-point $D_\ell$ values via eqn (1) (see Tables 1–3, respectively).
Finally, it has been shown\textsuperscript{96} that $k_\circ$ values for complexes $B \cdot HX$ can be predicted with the aid of eqn (12)

$$k_\circ = \epsilon' N_B E_{XY},$$

(12)

where $\epsilon'$ 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\textsuperscript{97} holds when the Lewis acids are dihalogen molecules. In view of the direct proportionality $D_B = c_B k_\circ$ established here, it follows that it is also possible to use $D_B$ values in a similar manner to establish nucleophilicities for Lewis bases $B$ and electrophilicities for Lewis acids $HX$ or $XY$.

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