

Determination of stretching force constants of weakly bound dimers from centrifugal distortion constants

D. J. MILLEN

Christopher Ingold Laboratories, Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ, England

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This paper is dedicated to Professor Camille Sandorfy on the occasion of his 65th birthday

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Expressions are derived from which stretching force constants for the weak bond in weakly bound dimers may be evaluated directly from observed rotational constants and centrifugal stretching distortion constants.

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On a dérivé des expressions à partir desquelles on peut évaluer les constantes de force d'élongation pour la faible liaison dans des dimères faiblement liés; cette évaluation peut se faire directement à partir des constantes rotationnelles observées et des constantes de distortion lors de l'élongation des liaisons par force centrifuge.

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Introduction

In recent years stretching force constants have been obtained for many weakly bound dimers. In some cases such force constants have been determined in the well-established way from vibrational wavenumbers associated with the stretching modes of the weakly bound dimer (1). In the majority of cases, however, they have been determined from the centrifugal distortion constant D_J since the information available is limited, by the experimental technique employed, to properties of the vibrational ground state (2, 3). Often a pseudo-diatomic model, which is equivalent to regarding each monomer as a point mass, has been used although it has been pointed out that this model is found to be satisfactory only when moments of inertia of the constituent monomers are small (4). Expressions have been obtained when this restriction is relaxed and allowance made for the inertial properties of the monomers for the specific case of a linear triatomic dimer (5) and for other particular cases (4), although these latter expressions contain a geometrical parameter which refers to the distance between the monomer units in the dimer. The present paper derives expressions in a general manner, for various classes of dimer, in a form which can be used for the evaluation of force constants directly from centrifugal distortion constants and rotational constants without introducing any structural parameters or indeed any assumption about internuclear distances in the dimer. It is clearly advantageous for such purposes as the comparison of force constants for series of hydrogen bonded dimers if force constants are evaluated from expressions not limited by the pseudo-diatomic approximation. Indeed, in some cases force constants free of this limitation have already been reported (4, 6).

Results and discussion

Dimers of the general type to be examined are conveniently denoted as $B \cdots H-A$. The proton donor $H-A$ may be a diatomic molecule, e.g. HF, HCl, or a polyatomic linear molecule, e.g., HCN, $H-C \equiv C-H$. The acceptor B is taken in turn to be a linear molecule, a symmetric top, and then cases are examined where B is a planar asymmetric top, first with HA in the plane of the asymmetric top and then with HA perpendicular to the plane of the asymmetric top. The model employed throughout regards force constants for distortions which contribute to D_J , other than the force constant for the stretching of

the weak bond, to be so large by comparison with the stretching force constant of the weak bond that all distortions other than stretching of the weak bond can be neglected. Thus for a linear dimer where D_J , measured as a frequency, is given by

$$[1] \quad D_J h = \frac{\hbar^4}{8I^4} \sum_{ij} J_{xx}^{(i)} (f^{-1})_{ij} J_{xx}^{(j)}$$

in which I is the principal moment of inertia, $J_{xx}^{(i)} = \partial I_{xx} / \partial R_i$, where R_i is the i th internal co-ordinate and $(f^{-1})_{ij}$ is the ij th compliance constant, all the $(f^{-1})_{ij}$ which contribute to D_J are put to zero except for the compliance constant which refers to the stretching of the weak bond.

The derivations use relationships between moments of inertia of dimer and monomers as for rigid bodies and so the expressions obtained will be strictly applicable to equilibrium rotational constants. The use of ground state rotational constants may lead to significant deviation where vibration-rotation constants α arise which are significant by comparison with rotational constants, as for example for large amplitude bending or stretching modes of very weakly bonded dimers.

Triatomic linear dimers $B \cdots H-A$

A number of dimers of this class have been studied, including for example $Ar \cdots HF$ (7) and also $Kr \cdots ClF$ (8). Geometrical parameters and masses for such a dimer are defined in Fig. 1. B is represented by the mass m_B while D and d refer to the distances of B from centres of masses of dimer and $H-A$ monomer, respectively. The principal moment of inertia of the dimer is given by

$$[2] \quad I_D = m_B D^2 + I_{HA} + m_{HA} (d - D)^2$$

where m_{HA} and I_{HA} refer to the mass and principal moment of inertia of HA. Substituting for D from the centre of mass condition we obtain

$$[3] \quad I_D = I_{HA} + \mu_D d^2$$

where

$$[4] \quad \frac{1}{\mu_D} = \frac{1}{m_B} + \frac{1}{m_{HA}}$$

Now if we use eq. [3] to insert into eq. [1] the single term that arises in the model, namely, that for stretching the weak intermolecular bond for which the force constant is k , the result is

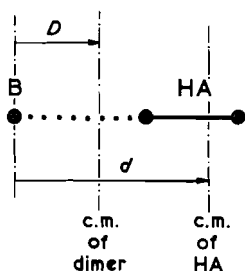


FIG. 1. Geometrical parameters and masses for triatomic linear dimers.

$$[5] \quad D_J h = \frac{\hbar^4}{2I_D^4} \frac{\mu_D^2 d^2}{k}$$

Finally eliminating d from this equation by using eq. [3] leads to

$$[6] \quad k = \frac{16\pi^2 \mu_D B_D^3}{D_J} \left(1 - \frac{B_D}{B_{HA}}\right)$$

where B_D and B_{HA} are the rotational constants for the dimer $B \cdots HA$ and for the monomer HA , respectively. If the stretching frequency ω of the dimer is assumed to be given as for a diatomic molecule, that is, if coupling with the $H-A$ stretching motion through the stretching force constant for this bond and the cross term in the potential function are ignored, then eq. [6] leads to

$$[7] \quad D_J = \frac{4B_D^3}{\omega^2} \left(1 - \frac{B_D}{B_{HA}}\right)$$

an equation which has been obtained by Novick (5) using an alternative derivation for the particular case of the triatomic dimer. The equation reduces to the well known expression for the pseudo-diatomic case

$$[8] \quad D_J = \frac{4B_D^3}{\omega^2}$$

when $B_{HA} \gg B_D$.

Polyatomic linear dimer

The geometrical parameters required for discussion of the general case are defined in an analogous way to those for the triatomic dimer and are shown in Fig. 2. In this case the principal moment of inertia of the dimer is given by

$$[9] \quad I_D = I_B + m_B D^2 + I_{HA} + m_{HA} (d - D)^2$$

where m_B and I_B are the mass and principal moment of inertia of B . Proceeding as before we obtain

$$[10] \quad D_J h = \frac{\hbar^4}{2I_D^4} \frac{\mu_D^2 d^2}{k}$$

In this case $\mu_D d^2$ is given by

$$[11] \quad \mu_D d^2 = I_D \left(1 - \frac{I_{HA} + I_B}{I_D}\right)$$

and hence the force constant k is given by

$$[12] \quad k = \frac{16\pi^2 \mu_D B_D^3}{D_J} \left(1 - \frac{B_D}{B_{HA}} - \frac{B_D}{B_B}\right)$$

When B is a point mass eq. [12] reduces to eq. [6]. The conditions under which this expression reduces to that for the pseudo-diatomic model are seen to be $B_{HA} \gg B_D$ and $B_B \gg B_D$.

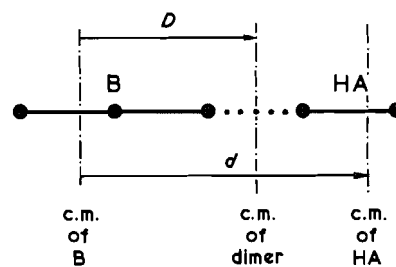


FIG. 2. Geometrical parameters and masses for polyatomic linear dimers.

Symmetric top dimers

Numerous examples of symmetric top dimers such as $CH_3CN \cdots HF$ (9), $PH_3 \cdots HCl$ (10), and $H_3N \cdots H-C \equiv C-H$ (11) have been examined. The parameters D and d are defined again as in Fig. 2. D and d are related through the centre of mass condition.

$$[13] \quad \sum_B m_i (z_i - D) + \sum_{HA} m_j (z_j + d - D) = 0$$

where z refers to the symmetry axis of the top. These lead to

$$[14] \quad D = \frac{m_{HA} d}{m_B + m_{HA}}$$

and making use of the expression for a symmetric rotor (16)

$$[15] \quad D_J h = -\frac{\hbar^4}{4} \tau_{xxxx}$$

we obtain

$$[16] \quad k = \frac{16\pi^2 \mu_D B_D^3}{D_J} \left(1 - \frac{B_D}{B_{HA}} - \frac{B_D}{B_B}\right)$$

An alternative expression (4) has been obtained by a similar derivation for symmetric tops, but the present expression has the advantage of allowing calculation of k directly from the centrifugal distortion constants and rotational constants without requiring the evaluation of any structural parameter of the dimer.

Asymmetric top dimers

Planar asymmetric top dimers with C_{2v} symmetry

Examples of this group of dimer are formed by $H-C \equiv C-H$ with HF (12) and HCl (13), and the group may be extended to include $H_2O \cdots HF$ (14) and $H_2O \cdots HCl$ (15), which are effectively planar. The parameters D and d are defined in an analogous way to that in Fig. 2. If we take the case where the symmetry axis z is the a -axis, we have for the principal moments of inertia about the b - and c -axes

$$[17] \quad I_D^b = I_B^b + I_{HA} + \mu_D d^2$$

and

$$[18] \quad I_D^c = I_B^c + I_{HA} + \mu_D d^2$$

In this case it has been shown (16)

$$[19] \quad D_J h = -\frac{\hbar^4}{32} (3\tau_{bbbb} + 3\tau_{cccc} + 2\tau_{ccbb})$$

Following the procedure as before we obtain

$$[20] \quad D_J h = 16\pi^4 \mu_D^2 d^2 k^{-1} [4B_D^4 + 4C_D^4 - (B_D - C_D)^2 (B_D + C_D)^2]$$

which, when combined with eqs. [17] and [18], leads to

$$[21] \quad k = \frac{8\pi^2\mu_D}{D_J} [B_D^3(1-b) + C_D^3(1-c) - \frac{1}{4}(B_D - C_D)^2(B_D + C_D)(2-b-c)]$$

where

$$[22] \quad b = \frac{B_D}{B_B} + \frac{B_D}{B_{HA}}$$

and c is given by an analogous expression. In the case when $B_D = C_D$ eq. [21] reduces to eq. [12].

Asymmetric top dimers with hydrogen bond perpendicular to planar monomer

Dimers of this kind include hydrogen bonded complexes formed by $H_2C=CH_2$ with HF (17) and HCl (18). The parameters D and d now refer to the distance along the z -direction of the molecular plane of B from the centres of mass of dimer and HA respectively. I_D^b and I_D^c are again given by eqs. [17] and [18]. The centrifugal distortion constant Δ_J is given by (19).

$$[23] \quad \Delta_J h = -\frac{\hbar^4}{8} (\tau_{xxxx} + \tau_{yyyy})$$

and following the procedures used previously we obtain

$$[24] \quad \Delta_J h = 64\pi^4 \mu_D^2 d^2 k^{-1} [B_D^4 + C_D^4]$$

Substituting for $\mu_D d^2$ from eqs. [17] and [18] leads to

$$[25] \quad k = \frac{8\pi^2\mu_D}{\Delta_J} [B_D^3(1-b) + C_D^3(1-c)]$$

where b and c are defined as before. This expression is generally applicable to asymmetric rotor dimers with HA along a principal axis of inertia and thus also applies to planar dimers. It is seen from eq. [25] that significant deviations from the pseudo-diatomic model will arise when rotational constants for the dimer, B_D and C_D , are not small by comparison with B and C values for either of the constituent monomers of the dimer.

Discussion

Expressions have been obtained which relate stretching force constants for the weak bond in weakly bound dimers to centrifugal stretching distortion constants. The expressions, which are free of limitations of the pseudo-diatomic model, are in a convenient form for direct application to dimers $B \cdots HA$ of linear and symmetric rotor types and also to certain asymmetric rotor types. Calculations have already been made (4) which show that use of the pseudo-diatomic model can lead to significant

error in the force constant k as a consequence of neglecting the inertial properties of the components which constitute the dimer. Other calculations have been made which show that the expressions obtained lead to consistent results when applied to a series of molecules (6), to series of several isotopic species of a linear dimer, $N_2 \cdots HCN$ (20), and to a series of several isotopic species of an asymmetric rotor dimer, $H_2O \cdots HCN$ (21). Recent applications have also been made to the linear dimer $HC \equiv C - C \equiv N \cdots HF$ (22) and to the symmetric rotor $(CH_3)_3P \cdots HCN$ (23).

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