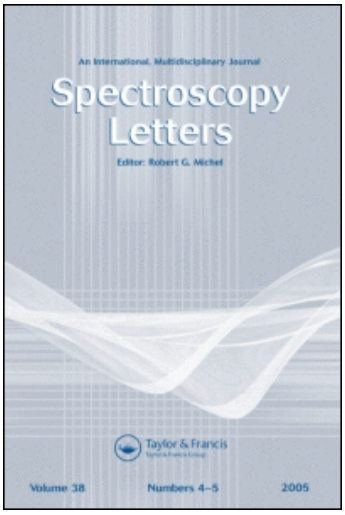

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Cartesian Dynamics of Simple Molecules I Diatomics and Centrosymmetric Triatomics

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CARTESIAN DYNAMICS OF SIMPLE MOLECULES
I DIATOMICS AND CENTROSYMMETRIC TRIATOMICS

Key Words: Molecular vibrations; infrared spectroscopy; Raman spectroscopy; lattice dynamics.

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ABSTRACT

A simple spring model for molecular vibrations is described in which Cartesian co-ordinates are used for both longitudinal and transverse displacements. The transverse restoring forces are shown to be electrostatic in origin and much weaker than the elastic longitudinal forces. The technique is applied to diatomic and centrosymmetric triatomic molecules. In the latter case, an analytical expression for the bending mode frequency is obtained which is equivalent to that derived by conventional methods using bending constants and internal co-ordinates. The model offers certain advantages when applied to the dynamics of crystals, for which Cartesian co-ordinates, aligned with the unit cell axes, are the natural choice. Reference is made to recent work on molecular and ionic crystals using extensions of this model.

INTRODUCTION

In a recent series of papers from this laboratory, the lattice dynamics of simple molecular crystals have been presented in terms of simple spring constant models[1-4]. A feature of this

approach is that splittings of internal molecular modes are calculated in addition to the lattice mode frequencies, since a unified approach is used for both inter- and intra-molecular interactions. In the more conventional method, which involves intermolecular potential functions, the rigid molecule approximation is usually adopted. In developing the spring constant models, we have found that a cartesian approach is most suitable for analysing the normal modes of the unit cell, since atomic displacements are usually expressed in terms of vectors parallel to these axes. Similarly, a comparison of unit cell modes with those of the isolated molecule is most conveniently accomplished in terms of cartesian co-ordinates. An offshoot of these lattice dynamics calculations has therefore been the development of analytical expressions for the normal mode frequencies of simple molecules in purely cartesian form, instead of the usual one involving internal co-ordinates such as bond lengths and angles.

In this report, the principles of the method will be described and its equivalence to other approaches established by comparing the expressions obtained for diatomic and triatomic linear molecules. In particular, the treatment of bending modes is presented in terms of electrostatic interactions expressed in cartesian form, subject to the constraint that there are no restoring forces involved for the pure rotation of an isolated molecule. From the observed frequencies of the normal modes by

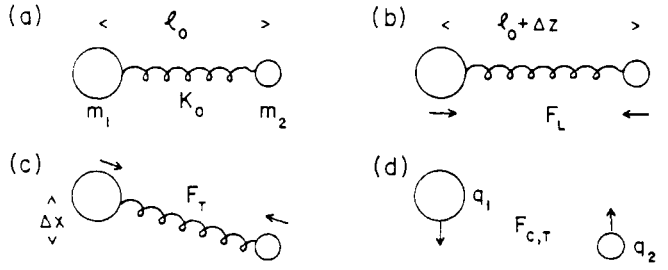

FIG. 1 Model of Diatomic Molecule.
(a) At equilibrium; length ℓ_0, spring constant k_0.
(b) Longitudinal displacement, Δz; $F_c = -k_0 \Delta z$.
(c) Transverse displacement, Δx; $F_T = -k_0 \Delta x^2 / 2\ell_0$.
(d) Transverse Coulombic Force: $F_{c,T} = -\delta \Delta x$.

Raman and infrared spectroscopy, principal force constants are calculated for these simple molecules.

DESCRIPTION OF THE MODEL

We consider first the interactions between two atoms. The short range elastic contribution may be represented by a longitudinal spring obeying Hooke's law, with force constant k_0, as shown in Figure 1. For displacements parallel to this spring, a longitudinal restoring force, $F_L = -k_0 \Delta z$, is set up on each atom. For perpendicular or transverse displacements, however, the extension of the spring is approximately $\Delta x^2 / 2\ell_0$, where ℓ_0 is the equilibrium separation, and so no first order (harmonic) restoring force is created. There will also be an electrostatic contribution, which may be approximately represented by placing

point charges on the atoms. The Coulombic force in this case is given by

$$F_{C,L} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{\ell_0^2}$$

This will be attractive or repulsive depending on whether the charges have opposite or identical signs, respectively. The net effect will be to slightly change the equilibrium separation between the atoms until a balance between elastic and electrostatic forces is achieved. Longitudinal displacements from this new equilibrium position lead to oscillations controlled by a slightly modified force constant, k, which includes the weak electrostatic contribution.

In contrast to the purely elastic case, transverse displacements of atoms with charges of opposite sign do lead to first order restoring forces of the form,

$$F_{C,T} = - \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2 \Delta x}{\ell_0^3} = - \delta \Delta x$$

where δ represents an "electrostatic force constant", generally much weaker than the longitudinal elastic force constant, k. These transverse force constants are subject to constraints, since for pure rotations there can be no restoring forces. Only for distortions from the linear configuration (that is, bending modes) will finite restoring forces be generated.

APPLICATION TO DIATOMIC MOLECULES

We consider first the simple case of a diatomic molecule, AB, with atoms of mass m_1 and m_2 and an equilibrium separation ℓ.

There are 6 degrees of freedom, of which 3 correspond to pure translations and 2 to pure rotations. The only internal mode is that corresponding to stretching and compressing the longitudinal spring, with Hooke law constant k. The equations of motion for displacements along the molecular axis have the following form:

$$m_1\ddot{z}_1 = -k\left(z_1 - z_2\right) \quad \text{and} \quad m_2\ddot{z}_2 = -k\left(z_2 - z_1\right)$$

For harmonic oscillations, $z_n = z_{no} \cos \omega t$ and

$$\ddot{z}_n = -\omega^2 z_{no} \cos \omega t = -\omega^2 z_n$$

We therefore obtain two coupled linear equations in z_1 and z_2.

$$m_1\omega^2 z_1 - k\left(z_1 - z_2\right) = 0 \quad \text{and} \quad m_2\omega^2 z_2 - k\left(z_2 - z_1\right) = 0$$

The secular determinant has the form

$$\begin{vmatrix} m_1\omega^2 - k & k \\ k & m_2\omega^2 - k \end{vmatrix} = 0$$

which gives for the eigenfrequencies $\omega_0 = 0$ (corresponding to a pure translation of the whole molecule) and

$$\omega_1 = (k/\mu)^{1/2} \quad \text{with } \mu = m_1 m_2/(m_1+m_2) \tag{1}$$

(corresponding to the stretching mode, in which the two atoms move with opposite phase and with amplitudes such that the centre of mass is stationary). For heteropolar diatomics ($m_1 \neq m_2$), this motion will result in an oscillatory dipole and the mode will be infrared active.

For homopolar molecules, $m_1 = m_2 = m$, and equation (1) reduces to

$$\omega_1 = \left(2k/m\right)^{1/2} \tag{2}$$

No dipole change is involved in this case, but there will be an

oscillatory change in the polarizability and the vibration may be observed in the Raman effect.

We next consider transverse displacements, in the x direction, say. The equations of motion are very similar to those for the longitudinal case:

$$m_1\ddot{x}_1 = \delta\left(x_1 - x_2\right) \quad \text{and} \quad m_2\ddot{x}_2 = -\delta\left(x_2 - x_1\right).$$

In addition to the pure translational mode $\left(x_1 = x_2\right)$, there is a second zero frequency mode corresponding to a pure rotation. In this case, $x_1 = -x_2$ and $\ddot{x}_1 = \ddot{x}_2 = 0$. The above equations are satisfied only if $\delta = 0$, and so the transverse motion is trivial in this case. For triatomic and other more complex molecules, it will be shown that application of these simple principles leads to non-zero transverse force constants and bending frequencies.

APPLICATION TO CENTROSYMMETRIC TRIATOMIC LINEAR MOLECULES

In the case of ABA linear molecules there are $3n - 5 = 4$ internal degrees of freedom. These comprise 2 stretching modes involving displacements along the molecular axis and a doubly degenerate bending mode involving transverse displacements. For these 3 frequencies, we will use 3 independent force constants to model the system. As shown in Figure 2, k_1 represents the 2 A-B bonds and k_2 the A-A interaction, with the expectation that $k_2 \ll k_1$. The equations of motion for longitudinal displacements are as follows:

$$m_1\ddot{z}_1 = -k_1\left(z_1 - z_2\right) - k_2\left(z_1 - z_3\right)$$

$$m_2\ddot{z}_2 = -k_1\left[z_2-z_1\right] - k_1\left[z_2 - z_3\right]$$

$$m_1\ddot{z}_3 = -k_1\left[z_3-z_2\right] - k_2\left[z_3 - z_1\right]$$

The secular determinant could now be derived and solved as in the diatomic case. However, a simplification results if it is recognized that the normal modes will involve displacements of the outside atoms which are equal in amplitude and either in or out of phase. We define $q_1 = x_1 + x_3$; $q_3 = x_1 - x_3$; and $q_2 = x_2$.

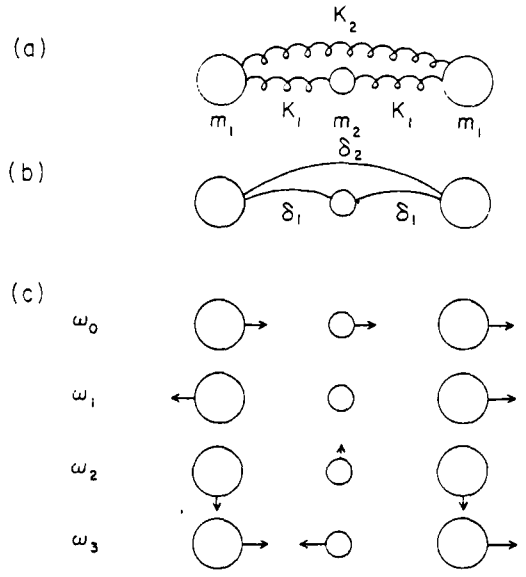

FIG. 2 Model of Centrosymmetric Triatomic Molecule.
(a) Longitudinal Springs, k_1,k_2.
(b) Transverse Springs, δ_1, δ_2.
(c) Form of Normal Modes.

Manipulation of the above three equations leads to the following:

$$m_1\ddot{q}_1 = -k_1\left(q_1 - 2q_2\right)$$

$$m_2\ddot{q}_2 = -k_1\left(2q_2 - q_1\right)$$

$$m_1\ddot{q}_3 = -k_1 q_3 - 2k_2 q_3$$

The equations form a "blocked" secular determinant:

$$\begin{vmatrix} m_1\omega^2-k_1 & 2k_1 & 0 \\ k_1 & m_2\omega^2-2k_1 & 0 \\ 0 & 0 & m_1\omega^2-k_1-2k_2 \end{vmatrix} = 0$$

The allowed eigenfrequencies are then easily deduced as follows:

From the lower [1 x 1] block, $\omega_1^2 = \left(k_1 + 2k_2\right)\Big/ m_1$ (3)

From the upper [2 x 2] block, we obtain after some algebraic manipulation, $\omega_0 = 0$

and $$\omega_3^2 = k_1\left(\frac{1}{m_1} + \frac{2}{m_2}\right) \qquad (4)$$

The mode corresponding to ω_0 is the pure translation of the whole molecule; ω_1 is the Raman active symmetric stretch, in which the central atom is stationary so that m_2 does not appear in equation (3); and ω_3 is the infrared active asymmetric stretch, in which the 2 outside atoms move in phase, so that k_2 does not appear in equation (4). The numerical subscripts used for the eigenfrequencies follow the convention used by Herzberg[5]. In this, ω_2 corresponds to the bending mode, for which the analysis follows.

For transverse displacements, we introduce 2 force constants, δ_1 and δ_2, indicated by bow symbols in Figure 2. The

analysis is identical to that for the stretching modes, with δ's replacing k's. However, in addition to the zero frequency translational mode, the condition for a pure rotation leads to a relation between δ_1 and δ_2. The equation of motion for x_1 has the form

$$m_1\ddot{x}_1 = -\delta_1\left(x_1 - x_2\right) - \delta_2\left(x_1 - x_3\right).$$

For a pure rotation, we let $x_1 = -x_3$ and $x_2 = 0$, and have $\ddot{x}_1 = 0$, since there is no restoring force. Substitution in the above equation leads to the following result: $\delta_2 = -\delta_1/2$

The eigenvalue equation corresponding to (3) above, therefore, has zero frequency, since $\left(\delta_1 + 2\delta_2\right) = 0$. The opposite signs of δ_1 and δ_2 fit our interpretation of their origins in electrostatic interactions, when one considers the charges on the atoms involved. The bending mode is represented by equation (4) above, suitably modified:

$$\omega_2^2 = \delta_1\left(\frac{1}{m_1} + \frac{2}{m_2}\right) = -2\delta_2\left(\frac{1}{m_1} + \frac{2}{m_2}\right) \qquad (5)$$

This result is identical to that given by Herzberg[5], if his k_δ is equal to $\delta_1/2\ell^2$, where ℓ is the A-B bond length. This mode generates an oscillatory dipole perpendicular to the molecule and may be observed as an infrared absorption.

RESULTS

In Table 1, the observed stretching frequencies of a number of heteropolar diatomic molecules are listed, together with values of the force constant k, calculated from equation (1). The working units of k, derived from masses expressed in atomic

TABLE 1

Heteropolar Diatomic Molecules
Observed Stretching Frequencies and Calculated Force Constants

Molecule	Frequency (cm^{-1})*	Force Constant (u cm^{-2})
HCl	2885.9	8.163×10^6
HBr	2559.3	6.520×10^6
HI	2230.1	4.973×10^6
HF	3961.6	1.502×10^7
NO	1875.9	2.628×10^7
CO	2143.2	3.151×10^7
IBr	265	3.443×10^6
ICl	381	4.023×10^6

* From Ref. 5.

TABLE 2

Homopolar Diatomic Molecules
Observed Stretching Frequencies and Calculated Force Constants

Molecule	Frequency (cm^{-1})*	Force Constant (u cm^{-2})
H_2	4160.2	8.723×10^6
N_2	2330.7	3.804×10^7
O_2	1554.7	1.934×10^7
F_2	892	7.558×10^6
Cl_2	556	5.480×10^6
Br_2	321	4.053×10^6
I_2	213	2.879×10^6

* From Ref. 5.

TABLE 3

Centrosymmetric Triatomic Molecules
Observed Vibrational Frequencies and Calculated Force Constants

Molecule	Frequencies (cm^{-1})*			Force Constants(ucm^{-2})		
	ω_1	ω_2	ω_3	k_1	k_2	δ_1
CO_2	1333	667	2349	2.407×10^7	2.180×10^6	1.943×10^6
CS_2	658	397	1535	1.192×10^7	9.822×10^5	7.972×10^5
CSe_2	368	308	1303	9.476×10^6	6.087×10^5	5.294×10^5

* From Refs. 6, 7.

mass units (u) and frequencies in wavenumbers (cm^{-1}), are ucm^{-2}. These can be converted to standard units by multiplying the table entries by 5.90×10^{-5} for N/m or by 5.90×10^{-2} for dyne/cm. Similar listings for homopolar diatomics are given in Table 2, where equation (2) has been used to calculate k. For centrosymmetric triatomic molecules, observed vibrational frequencies are listed in Table 3, together with values of the force constants k_1, k_2 and δ_1, calculated from equations (3), (4) and (5).

A useful test of the spring constant model for these molecules is provided by a comparison of the observed and calculated normal mode frequencies for isotopic species. These modes are observed as weak satellite peaks in the Raman and infrared spectra of naturally occurring samples, usually close to and on the low frequency side of the strong fundamentals of the main species. Spectra of enriched samples and of fully deuterated molecules are also often recorded. In solid state spectroscopy, it is important to distinguish peaks resulting from isotopic species from those caused by crystal field effects. In general, excellent agreement is obtained for these isotopic shifts, especially if proper account is taken of small anharmonic corrections, as discussed by Herzberg[5].

DISCUSSION

The expressions derived for the normal mode frequencies of these simple molecules are completely equivalent to those

obtained by previous workers. The simple spring model gives an excellent representation of the normal vibrations of these molecules, as confirmed by the good agreement found for the isotopic species. Interesting trends in the magnitudes of the force constants for series of molecules such as the hydrogen halides and the halogens may be observed in Tables 1 and 2 respectively. For the mixed halogens, ICl and IBr, the force constants lie between those of the corresponding homopolar halogens. For the triatomics, as expected, k_2 is much less than k_1 in all cases, because of the larger separations between interacting atoms. The transverse force constants, δ_1, are even smaller than k_2, a consequence of their electrostatic rather than elastic origins.

The model has been extended and applied to crystals of the three types of molecules discussed in this paper. Although numerical rather than analytical solutions are obtained in these cases, the model successfully predicts the lattice frequencies and crystal field splittings of the internal modes with the use of relatively few force constants. For the hydrogen halide crystals HF, HCl and HBr[2], which have isomorphous structures at low temperatures, the trend of decreasing hydrogen bond strengths with increasing halogen mass was confirmed, and the effects of weak intermolecular transverse force constants were investigated. For the halogen crystals, Cl_2, Br_2 and I_2[1], which are also isomorphous, the nearest neighbour intermolecular forces were

found to increase from Cl_2 to I_2 as a result of their increasingly covalent nature. The vibrations of solid CS_2, which is isomorphous to the halogens, were also successfully reproduced by the spring constant model[3]. All of the above unit cells are orthorhombic. A paper in preparation describes the application of the model to the cubic crystals α - N_2 and CO_2. The tetrahedral molecule $SnBr_4$, which forms a monoclinic crystal, has also been successfully modelled with these techniques[4].

Extension to ionic crystals such as the alkali cyanides[8] and layered compounds of the $CdCl_2$ or CdI_2 types[9-12] has also been successful. In the latter case, analytical solutions were obtained, very similar to those derived for triatomic molecules in this paper. This is because for these structures, the normal modes involve motions of the ionic layers treated as rigid units and strongly resemble those of ABA molecules, weakly coupled to form linear chains.

In future papers, the techniques outlined here will be applied to more complex molecules. It will be shown that the use of Cartesian coordinates and combinations of longitudinal and transverse force constants lead to results which are identical to those derived by more conventional techniques and in some cases allow extensions to be made to the analytical expressions. The second paper in this series will discuss non-centrosymmetric linear triatomic molecules.

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