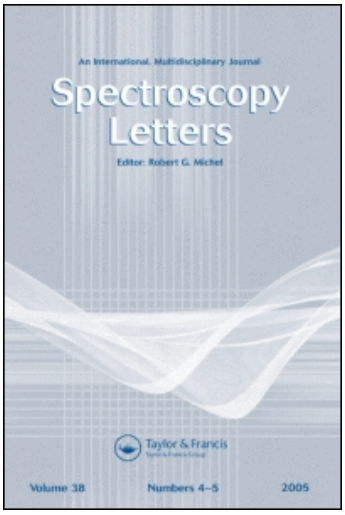

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Cartesian Dynamics of Simple Molecules II Non-Centrosymmetric Linear Triatomics

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CARTESIAN DYNAMICS OF SIMPLE MOLECULES
II NON-CENTROSYMMETRIC LINEAR TRIATOMICS

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

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ABSTRACT

A simple spring model for molecular vibrations, which uses Cartesian co-ordinates for both longitudinal and transverse displacements, is applied to non-centrosymmetric linear triatomic molecules. Analytical expressions for the stretching and bending mode frequencies are obtained, which are equivalent to those derived by conventional methods. For most molecules, the effects of the interaction between the outside atoms are shown to be negligible, but for N_2O, complex solutions are obtained unless this is included. The validity of the model is demonstrated by the satisfactory agreement between calculated and observed frequencies of isotopic species. For N_2O, frequency shifts resulting from isotopic substitution are explained by reference to the calculated eigenvectors.

INTRODUCTION

In a previous paper[1], a simple spring model for molecular vibrations which uses Cartesian co-ordinates was described and applied to diatomic and centrosymmetric triatomic molecules.

This approach was shown to be equivalent to the usual one involving internal co-ordinates, such as bond lengths and angles, and intrinsically more suitable for extensions to lattice dynamics calculations[2-6]. In this communication, the model is extended to the case of linear triatomic molecules which lack a centre of symmetry.

Analytical expressions are derived for the normal mode frequencies of these molecules, and the principal force constants are evaluated with the use of data from the observed Raman and infrared spectra. In addition, it is shown that additional spectroscopic information from isotopic molecules may in principle be utilised to obtain estimates of the smaller force constant modelling the interaction between the two outside atoms.

The geometry for these molecules, which have point group $C_{\infty v}$, is shown in Figure 1 (a). They may be categorized as ABC type molecules, but A and B may be the same, as in N_2O. There are 9 degrees of freedom, of which 3 correspond to pure translations and 2 to pure rotations. The remaining 4 internal degrees of freedom correspond to 2 stretching modes (ν_1 and ν_3, σ^+ species) involving displacements along the molecular axis, and a doubly degenerate bending mode (ν_2, π species) in which the displacements are perpendicular to this axis. All modes involve both dipole and polarizability changes and so are active in both infrared and Raman spectra. The approximate form of the normal modes is shown in Figure 1 (b).

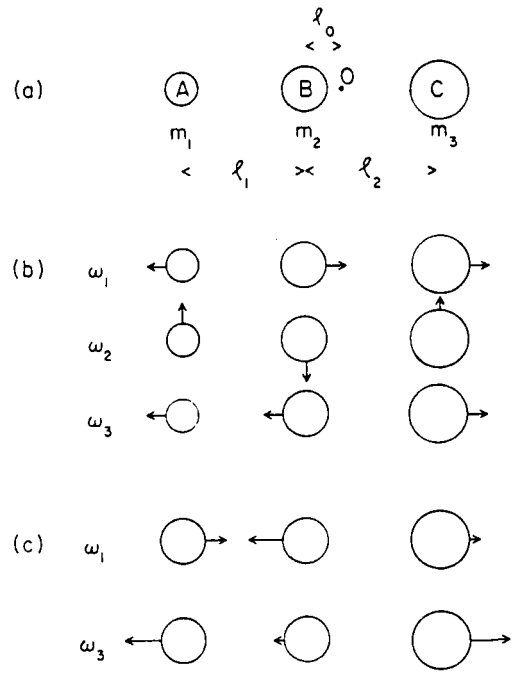

FIG. 1 Geometry and Normal Modes of ABC Linear Molecules
(a) Geometry, showing masses, bond lengths and centre of mass, O.
(b) Typical normal modes, with ω_1 the A-B stretch, ω_2 the bend, and ω_3 the B-C stretch.
(c) Eigenvectors for N_2O, with ω_1 the asymmetric stretch and ω_2 the symmetric stretch (see text).

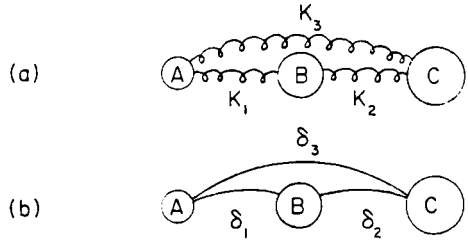

FIG. 2 Spring Constant Model for ABC Linear Molecules
(a) Longitudinal Springs K_1, K_2 and K_3.
(b) Transverse springs δ_1, δ_2 and δ_3.

DESCRIPTION OF THE MODEL

We first consider the motion along the molecular z-axis and derive expressions for ν_1 and ν_3. Following the principles outlined in the first paper of this series[1], we introduce longitudinal springs K_1, K_2 and K_3 as shown in Figure 2 (a). The equations of motion in the z direction for the 3 atoms, according to Newton's second law and Hooke's law, are as follows:

$$m_1\ddot{z}_1 = -K_1\left(z_1 - z_2\right) - K_3\left(z_1 - z_3\right)$$

$$m_2\ddot{z}_2 = -K_1\left(z_2 - z_1\right) - K_2\left(z_2 - z_3\right)$$

$$m_3\ddot{z}_3 = -K_2\left(z_3 - z_2\right) - K_3\left(z_3 - z_1\right)$$

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

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

Substitution leads to 3 coupled linear equations of the following form:

$$m_1\omega^2 z_1 - K_1\left(z_1 - z_2\right) - K_3\left(z_1 - z_3\right) = 0$$

$$m_2\omega^2 z_2 - K_1\left(z_2 - z_1\right) - K_2\left(z_2 - z_3\right) = 0$$

$$m_3\omega^2 z_3 - K_2\left(z_3 - z_2\right) - K_3\left(z_3 - z_1\right) = 0$$

These equations lead to the following secular determinant:

$$\begin{vmatrix} m_1\omega^2 - K_1 - K_3 & K_1 & K_3 \\ K_1 & m_2\omega^2 - K_1 - K_2 & K_2 \\ K_3 & K_2 & m_3\omega^2 - K_2 - K_3 \end{vmatrix} = 0$$

When this determinant is expanded in the usual way, a power series in ω^2 is obtained of the form

$$A\omega^6 + B\omega^4 + C\omega^2 + D = 0 \qquad (1)$$

It is easily shown that D = 0, so that ω^2 is a factor. Hence ω = o is an allowed root, corresponding to a pure translation in the z direction $\left(z_{10} = z_{20} = z_{30}\right)$. The other two non-zero roots may be determined from the resulting quadratic equation in ω^2. Following Herzberg[7], we use the well-known expressions for the sum and product of these roots, ω_1 and ω_3, to obtain the following expressions for the eigenfrequencies:

$$\omega_1^2 + \omega_3^2 = -B/A = K_1\left(\frac{1}{m_1} + \frac{1}{m_2}\right) + K_2\left(\frac{1}{m_2} + \frac{1}{m_3}\right) + K_3\left(\frac{1}{m_1} + \frac{1}{m_3}\right) \qquad (2)$$

$$\text{and } \omega_1^2\omega_3^2 = C/A = \left(K_1K_2 + K_1K_3 + K_2K_3\right)\left(m_1 + m_2 + m_3\right)/m_1m_2m_3 \qquad (3)$$

It is expected that K_3, representing the interaction between the well-separated outer atoms, will be much smaller than K_1 and K_2. If it is neglected completely, the above equations reduce to the following:

$$\omega_1^2 + \omega_3^2 \approx K_1\left(\frac{1}{m_1} + \frac{1}{m_2}\right) + K_2\left(\frac{1}{m_2} + \frac{1}{m_3}\right) \qquad (4)$$

$$\text{and } \omega_1^2\omega_3^2 \approx K_1K_2\left(m_1 + m_2 + m_3\right)/m_1m_2m_3 \qquad (5)$$

Equations (4) and (5) are identical to those given by Herzberg[7]. It is clear that if ω_1 and ω_3 are known from spectroscopic measurements, K_1 and K_2 may be calculated. Furthermore, if frequencies for an isotopic molecule are available, in principle K_3 may also be found, with slight adjustments to the original values of K_1 and K_2.

For motion perpendicular to the molecular axis, we introduce transverse springs δ_1, δ_2 and δ_3, displayed in Figure 2(b) as bow

symbols. The equations of motion in the x or y direction are identical to those for the stretching modes with δ's replacing K's. However, in addition to the zero frequency pure translational mode, the condition for a pure rotation leads to relations between the δ's, which will now be derived.

For a linear triatomic ABC molecule with dimensions as shown in Figure 1 (a), we assume that the centre of mass, O, is a distance ℓ_0 from the middle atom, B. Then, for a pure rotation through an angle α about O, the transverse displacements are as follows:

$$x_1 = \left(\ell_1 - \ell_0\right)\alpha; \qquad x_2 = -\ell_0\alpha; \qquad x_3 = -\left(\ell_0 + \ell_2\right)\alpha$$

If we substitute these values into any two of the original equations of motion and in addition put the accelerations equal to zero (since there can be no net restoring forces for a pure rotation), we obtain the following relations between the transverse force constants:

$$\delta_1 = \delta_2\ell_2/\ell_1 = -\delta_3\left(1 + \ell_2/\ell_1\right) \tag{6}$$

Parenthetically, we note that for a centrosymmetric triatomic, $\left(\ell_1 = \ell_2\right)$, these reduce to $\delta_1 = \delta_2 = -2\delta_3$ as found in the earlier paper[1].

When the secular determinant obtained previously (with δ's replacing K's) is expanded, not only is the coefficient D of equation (1) equal to zero (giving a root $\omega = 0$ corresponding to a pure translation), but the expression for the coefficient C, given by

$$C = \left(\delta_1\delta_2 + \delta_1\delta_3 + \delta_2\delta_3\right)\left(m_1 + m_2 + m_3\right)/m_1m_2m_3$$

also reduces to zero, because of the relations between the δ's, equations (6). Hence a second root has $\omega = 0$, and this clearly corresponds to the pure rotation.

The remaining non-zero root is given by the equation

$$\omega_2^2 = \left(\delta_1 + \delta_3\right)/m_1 + \left(\delta_1 + \delta_2\right)/m_2 + \left(\delta_2 + \delta_3\right)/m_3$$

This may be expressed as a function of any one of the δ's, by using equations (6). The simplest form is in terms of δ_3:

$$\omega_2^2 = -\delta_3\left[\ell_2^2/m_1 + \left(\ell_1 + \ell_2\right)^2/m_2 + \ell_1^2/m_3\right]\Big/\ell_1\ell_2 \qquad (7)$$

This is equivalent to the expression given by Herzberg[7], if his $K_\delta = -\ell_1\ell_2\delta_3$. Clearly, if the bending mode frequency, ω_2, is measured spectroscopically and if the bond lengths of the molecule are known, δ_3 or K_δ can be evaluated directly.

RESULTS

For the simple case where K_3 is neglected, the 3 observed spectroscopic frequencies are sufficient to solve for the 3 principal force constants K_1, K_2 and δ_3. Values of these frequencies and the bond lengths ℓ_1 and ℓ_2 for a number of non-centrosymmetric linear triatomics are listed in Table 1. Corresponding values for the force constants, calculated from equations (4), (5) and (7), are given in Table 2. With these values of the force constants, normal mode frequencies for a number of isotopic molecular species may be calculated and compared with experimental values, as shown in Table 3.

It is known from similar calculations on centrosymmetric triatomics[1], that the force constant representing the interaction between the outside atoms, here designated K_3, is not negligible,

TABLE 1

Bond Lengths and Normal Mode Frequencies of ABC Linear Molecules*

Molecule	ℓ_1	ℓ_2	ω_1	ω_2	ω_3+
	(Å)			(cm^{-1})	
N_2O	1.15	1.23	2224	589	1285
OCS	1.16	1.54	2002	520	859
HCN	1.06	1.15	3310	712	2097
ClCN	1.76	1.15	774	378	2216
BrCN	1.93	1.15	575	342	2198
ICN	2.12	1.15	486	304.5	2188

*Data selected from Refs. 7, 8, +The usual notation has been changed so that ω_3 refers to the C-N stretch for all four cyanide molecules listed.

TABLE 2

Calculated Principal Force Constants of ABC Linear Molecules*

Molecule	K_1	K_2	$-\delta_3$
	($u\text{-}cm^{-2}$)		
N_2O	(complex values)		8.25×10^5
OCS	1.11×10^7	2.73×10^7	6.06×10^5
HCN	9.90×10^6	3.06×10^7	3.44×10^5
ClCN	9.19×10^6	2.87×10^7	3.00×10^5
BrCN	6.98×10^6	2.91×10^7	2.42×10^5
ICN	5.39×10^6	2.93×10^7	1.85×10^5

*Working units from $K = \mu\omega^2$ with μ (reduced mass) in atomic mass units (u) and ω in wavenumbers (cm^{-1}). Multiply table entries by 5.90×10^{-5} to convert to N/m or by 5.90×10^{-2} for dyne/cm. K_3 put equal to zero (see text).

TABLE 3

Comparison of Calculated and Observed Frequencies (cm^{-1}) for Isotopic Molecules

Molecule	Calculated Frequencies*			Observed Frequencies		
	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
^{2}HCN	2603	568	1925	2630	569	1925
$^{37}ClCN$	736	377.5	2215	736	378	2215
$^{35}Cl^{13}CN$	738.5	367	2162	738	367	2164
$^{37}Cl^{13}CN$	730	367	2162	730	367	2163
$^{81}BrCN$	573.5	342	2199.5	573	342	2198
$^{79}Br^{13}CN$	568.5	332	2148	568	332	2147
$^{81}Br^{13}CN$	567	332	2148	566	332	2147

*Using force constants listed in Table 2.

TABLE 4

Optimized Force Constants and Stretching Mode Frequencies for N_2O Isotopic Molecules

Molecule	Force Constants ($u\text{-}cm^{-2}$)		
	K_1	K_2	K_3
$^{14}N_2O$	2.698×10^{7}	1.896×10^{7}	1.547×10^{6}

	Frequencies (cm^{-1})			
	Calculated		Observed*	
	ω_1	ω_3	ω_1	ω_3
$^{14}N_2O$	2224	1285	2224	1285
$^{15}N^{14}NO$	2204	1267	2202.5	1271
$^{14}N^{15}NO$	2175	1284	2178	1281
$^{15}N_2O$	2154	1266	2156	1266

* Data from Ref. 10.

although always much smaller than those between bonded atoms. In order to estimate K_3 for ABC type molecules, we can in principle make use of the stretching frequencies from isotopic species, ω_1' and ω_3'. However, for all but one of these non-centrosymmetric molecules, it was found that a best fit to the four frequencies, ω_1, ω_3, ω_1' and ω_3', obtained from an optimization routine known as SIMPLEX[9], gave force constants similar to those in Table 2, that is with K_3 essentially zero. Only for the N_2O molecule was a finite value of K_3 required. In fact, in this case if $K_3 = 0$, complex values for K_1 and K_2 are obtained, which is clearly unacceptable from a physical viewpoint. We therefore adjusted the three stretching constants for the best fit for the $^{14}N_2O$ molecule and then used these values to calculate the frequencies for a number of isotopic species. The results of these computations are given in Table 4, which lists the optimized force constants and calculated frequencies, together with the observed values of Begun and Fletcher[10]. Of course, the value of the bending constant, δ_3, is not affected by these adjustments to the stretching constants.

DISCUSSION

It should first be pointed out that two distinct sets of values of K_1 and K_2 are obtained from equations (4) and (5). Both are mathematically valid and, superficially at least, physically reasonable, but inspection and comparison with data from other molecules allows the selection given in Table 2 to be made. It may be seen there that the bending constant is

appreciably smaller than the two stretching constants for all molecules. This was also the case for the centrosymmetric molecules discussed in an earlier paper[1], and interpreted as a consequence of the transverse restoring forces being electrostatic rather than elastic in origin. For the four cyanide molecules, the approximate constancy of the C-N stretching constant K_2 is noted, as are the decreasing strengths of the halogen-carbon stretching constants, K_1, and the bending constants, δ_3, with increasing halogen mass. The agreement between the calculated and observed isotopic frequencies listed in Table 3 is very satisfactory, indicating that the simple model used is acceptable for most purposes. Only for DCN is there a slight discrepancy for ω_1, and this may be readily explained as a result of different anharmonic contributions (neglected in this model) for the H and D motions. In the harmonic approximation, a slight increase in the value of the D-C force constant K_1, from 9.90×10^6 to 10.14×10^6 ucm^{-2}, is required to obtain agreement with the observed value of 2630 cm^{-1} for ω_1.

The case of the N_2O molecule is of particular interest. The optimized value of K_3, required to give non-complex solutions, is much smaller than K_1 and K_2, as expected, and similar in magnitude to the corresponding force constant in the centrosymmetric triatomics[1]. The calculated isotopic frequencies (Table 4) are in excellent agreement with observed values, indicating that this four parameter harmonic model is an acceptable representation of the vibrations of this molecule.

Some of the frequency changes resulting from isotopic substitution are, at first sight, somewhat surprising. For example, changing the outside N atom has an appreciable effect on ω_3, usually described as the N-O stretch[7], whereas changing the central N atom has negligible effect. The explanation of these phenomena is found in an examination of the eigenvectors. For N_2O, because of the similarity of the three atomic masses, the normal modes are similar to those for the centrosymmetric triatomics such as CO_2 (or N_2O if the atomic arrangement was N-O-N). The stretching modes are here described as symmetric and anti-symmetric, and in the former the central atom is static. For N_2O, the eigenvectors for ω_3 indicate a very small amplitude for the motion of the central N atom with larger and approximately equal and opposite displacements for the outside atoms. Conversely, for ω_1, the central atom has the largest displacement. The eigenvectors for N_2O are shown in Figure 1 (c). The calculated and observed frequency shifts on isotopic substitution are readily understandable in these terms. The labels N-N stretch and N-O stretch for ω_1 and ω_3, respectively, are clearly inappropriate for N_2O.

Although the vibrational spectra of these molecules in their crystalline states have been observed[11,12], relatively little work on their lattice dynamics has been published. All the molecules discussed above, except N_2O, form linear chains in the crystal, with one or two molecules per unit cell, and should be relatively simple systems to analyse, by using extensions of the

simple spring model discussed here and already applied to other molecular solids[2-6]. Work is planned in this laboratory on similar applications to these ABC type molecular crystals. The case of N_2O is different, as this forms a cubic crystal similar to that for CO_2, but with end-to-end disorder of the molecular orientation, and hence is difficult to model.

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