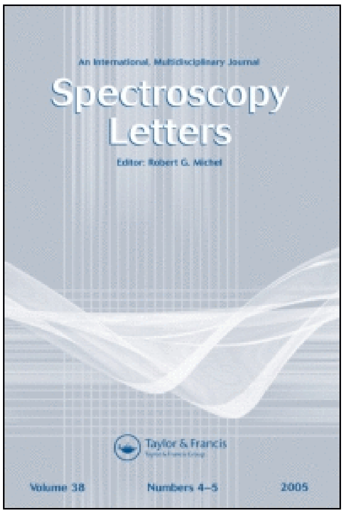

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Cartesian Dynamics of Simple Molecules III Non-Linear Triatomics (C_{2v} Symmetry)

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CARTESIAN DYNAMICS OF SIMPLE MOLECULES
III NON-LINEAR TRIATOMICS (C_{2v} SYMMETRY)

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

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ABSTRACT

A simple spring model for the molecular vibrations of non-linear triatomic molecules with C_{2v} symmetry is described in terms of Cartesian co-ordinates. Analytical expressions for the stretching and bending mode frequencies are obtained and compared with previous derivations. Optimized values of force constants are calculated for models involving two or three adjustable parameters. The validity of the model is demonstrated by the satisfactory agreement between calculated and observed frequencies of isotopic species. The model provides a simple explanation of the near degeneracy of the symmetric and asymmetric stretching frequencies of H_2S and H_2Se.

INTRODUCTION

In previous papers[1,2], a simple spring model for molecular vibrations, which is developed in terms of Cartesian

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co-ordinates, was described and applied to diatomic and triatomic linear molecules. This approach, which was shown to be equivalent to the usual method involving internal co-ordinates, offers certain advantages, when extensions to the lattice dynamics of molecular crystals are planned. In particular, crystal field splittings of internal molecular modes as well as frequencies of lattice modes may be obtained, using a uniform approach to intra- and inter-molecular interactions[3-7]. In this communication, the model is applied to the case of non-linear symmetric triatomic molecules such as sulphur dioxide or water.

Analytical expressions are derived for the normal mode frequencies of these molecules in terms of longitudinal and transverse force constants, atomic masses and bond angle. Values of these force constants are obtained by substitution of the observed Raman and infrared fundamental frequencies into the derived equations. The form of the normal modes is checked by calculating eigenvectors and confirming symmetry in the force constant matrix. The validity of the model is verified by comparing calculated and observed frequencies of various isotopic species.

The geometry for these AB_2-type molecules, which have point group C_{2v}, is shown in Figure 1(a). There are 9 degrees of freedom, of which 3 correspond to pure translations and another 3 to pure rotations. The remaining 3 internal degrees of freedom comprise the symmetric stretch, ω_1, and bend, ω_2, both of A_1

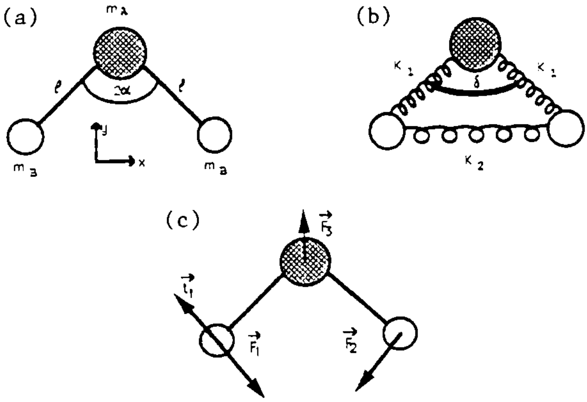

FIG. 1 Geometry and Interactions of AB_2 (C_{2v}) Molecules
(a) Geometry; (b) Longitudinal (K_1 and K_2) and Bending (δ) Force Constants; (c) For a displacement $\vec{t}_1$ perpendicular to the AB bond, a restoring force $\vec{F}_1$ and reaction forces $\vec{F}_2$ and $\vec{F}_3$ are set up, such that $\vec{F}_1 + \vec{F}_2 + \vec{F}_3 = 0$.

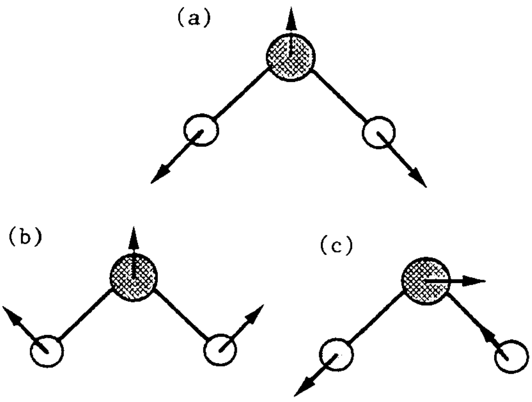

FIG. 2 Normal Modes of AB_2 (C_{2v}) Molecules.
(a) Symmetric stretch ω_1; (b) Bend ω_2;
(c) Asymmetric stretch ω_3.

species, and the asymmetric stretch, ω_3, of B_1 species. All 3 internal modes are active in both Raman and infrared spectra. These 3 observed frequencies may be used, in principle, to find values for 3 independent force constants. The approximate form of the 3 normal modes is shown in Figure 2. Because the symmetric stretch, ω_1, and the bend, ω_2, belong to the same species, some mixing will occur, the extent of which depends on the magnitudes of the corresponding force constants. This is in contrast to the case for linear molecules[1,2], where stretching and bending modes are completely decoupled.

DESCRIPTION OF THE MODEL

It may be readily shown that if the plane of the molecule is xy (see Figure 1(a)), the 3 degrees of freedom corresponding to motion in the z direction are all external modes (1 translation and 2 rotations). Hence, in order to obtain expressions for the internal modes, only motion in the xy plane need be considered. This leads to the development of a 6x6 matrix, the determinant of which has 3 zero roots, corresponding to 2 translations and 1 rotation, and 3 non-zero roots corresponding to the internal modes. The three force constants used in this model are K_1 for the principal AB stretching interactions, K_2 for the much weaker interaction between the B atoms, and δ for the resistance to changes in the molecular angle, 2α. These interactions are shown in Figure 1(b).

We first consider the restoring forces generated by the principal stretching constant, K_1. A displacement in the x direction by atom 1 causes a change in length of the spring, represented by K_1, and generates restoring forces in both the x and y directions. It is easy to show that the x-component is proportional to $\sin^2\alpha$ and the y-component to $\cos\alpha\sin\alpha$. Similarly, a displacement in the y direction by atom 1 generates restoring forces proportional to $\cos\alpha\sin\alpha$ for the x-component and $\cos^2\alpha$ for the y-component. By Newton's third law, equal and opposite reaction forces are produced on atom 3. Next, we consider the interaction between the two B atoms, represented by K_2. Clearly, only displacements in the x direction generate restoring forces and these only have x-components, independent of α. Finally, the angular force constant δ is considered. This is invoked when there are displacements perpendicular to the principal AB bonds. For example, for a displacement of atom 1 in the x direction, the component perpendicular to the bond is proportional to $\cos\alpha$, and the resultant restoring force F_1 has components proportional to $\cos^2\alpha$ in the x direction and $\cos\alpha\sin\alpha$ in the y direction. Reaction forces F_2 and F_3 are generated at atoms 2 and 3, as shown in Figure 1(c), with $\vec{F}_3 = \vec{F}_1 + \vec{F}_2$. This latter condition ensures that no external force or torque is generated for the molecule as a whole, which in turn guarantees that the pure translations and rotations have zero frequency. In a similar way, the restoring forces resulting from displacements of atoms 2 and 3 may be derived. In the latter case, it is easier to obtain the appropriate components by recognizing that a displacement of atom 3 is equivalent to equal and opposite displacements of both atoms 1 and 2.

The application of these ideas leads to 6 coupled linear equations, representing Newton's second law and Hooke's law, which have the following form:

$$m_B\ddot{x}_1 = -\left(K_1s^2 + K_2 + \delta c^2\right)x_1 + \delta csy_1 + \left(K_2 + \delta c^2\right)x_2 + \delta csy_2$$
$$+ K_1s^2x_3 + \left(K_1cs - 2\delta cs\right)y_3$$

$$m_B\ddot{y}_1 = \delta csx_1 - \left(K_1c^2 + \delta s^2\right)y_1 - \delta csx_2 - \delta s^2y_2 + K_1csx_3$$
$$+ \left(K_1c^2 + 2\delta s^2\right)y_3$$

$$m_B\ddot{x}_2 = \left(K_2 + \delta c^2\right)x_1 - \delta csy_1 - \left(K_1s^2 + K_2 + \delta c^2\right)x_2 + \left(K_1cs - \delta cs\right)y_2$$
$$+ K_1s^2x_3 + \left(2\delta cs - K_1cs\right)y_3$$

$$m_B\ddot{y}_2 = \delta csx_1 - \delta s^2y_1 + \left(K_1cs - \delta cs\right)x_2 - \left(K_1c^2 + \delta s^2\right)y_2 - K_1csx_3$$
$$+ \left(2\delta s^2 + K_1c^2\right)y_3$$

$$m_A\ddot{x}_3 = K_1s^2x_1 + K_1csy_1 + K_1s^2x_1 - K_1csy_2 - 2K_1s^2x_3$$

$$m_A\ddot{y}_3 = \left(K_1cs - 2\delta cs\right)x_1 + \left(K_1c^2 + 2\delta s^2\right)y_2 + \left(2\delta cs - K_1cs\right)x_2$$
$$+ \left(2\delta s^2 + K_1c^2\right)y_2 - \left(2K_1c^2 + 4\delta s^2\right)y_3$$

where $c = \cos\alpha$ and $s = \sin\alpha$. For harmonic oscillations, $x_1 = x_{10}\cos\omega t$, and so $\ddot{x}_1 = -\omega^2x_{10}\cos\omega t = -\omega^2x_1$. When this and similar substitutions for the other accelerations are introduced, the secular determinant for this symmetric matrix is obtained.

The expansion of this determinant and subsequent solution for the six allowed roots involve much tedious algebra. To avoid this, we have made use of MAPLE[8], an interactive system for symbolic mathematical calculation, developed by the Symbolic Computation Group of the University of Waterloo. Using the linear algebra package of this system, we have found the six roots of the secular determinant, as follows:

$$\omega_0 = \omega_0' = \omega_0'' = 0$$

$$\omega_3^2 = K_1(1 + 2m_B\sin^2\alpha/m_A)/m_B \tag{1}$$

$$\omega_1^2 + \omega_2^2 = K_1(1 + 2m_B\cos^2\alpha/m_A)/m_B + 2K_2/m_B$$
$$+ 2\delta(1 + 2m_B\sin^2\alpha/m_A)/m_B \tag{2}$$

$$\omega_1^2\omega_2^2 = 2(1 + 2m_B/m_A)(K_1\delta + 2K_2\delta\sin^2\alpha + K_1K_2\cos^2\alpha)/m_B^2 \tag{3}$$

There are three special cases of equations (1)-(3) which merit comment. If we put $\delta = 0$, equations (2) and (3) reduce to those given by Herzberg[9] for the central force case (with appropriate notation changes: $K_1 \rightarrow a_{11}$, $K_2 \rightarrow a_{33}$). On the other hand, if we put $K_2 = 0$, we obtain Herzberg's equations for the valence force case ($\delta \rightarrow K_\delta/\ell^2$). Finally, if we let $\alpha = 90^\circ$, we obtain the equations for a centrosymmetric triatomic linear molecule, as derived in an earlier paper in this series[1]. In this case, the quadratic equation for ω_1^2 and ω_2^2 factorizes and the symmetric stretching and bending modes decouple. These solutions are also equivalent to those given by Herzberg[9], with appropriate changes in notation. For the present general case, it is clear that substitution of the three observed fundamental frequencies should allow the three force constants, K_1, K_2 and δ, to be estimated.

RESULTS

Fundamental frequencies, atomic masses and bond angles for eight triatomic C_{2v} molecules are listed in Table 1. Values for the three force constants, K_1, K_2 and δ, calculated from equations (1) to (3) are given in Table 2. As can be seen, for many molecules, K_2 is very small and negative and probably physically insignificant. We have therefore put $K_2 = 0$ and adjusted the values of K_1 and δ to give the best agreement between the calculated and observed frequencies, using a Simplex optimization routine[11]. A measure of the adequacy of this two parameter model is the value of the percentage root mean square deviation, defined as follows:

$$\Delta = 100 \left[\sum_{i=1}^{n} \frac{1}{n} \left(\frac{\omega_{oi} - \omega_{ci}}{\omega_{oi}} \right)^2 \right]^{1/2}$$

where ω_{oi} are the observed frequencies, ω_{ci} the calculated frequencies and n the number of observables, in this case 3. The results of this analysis are given in Table 3. Finally, using the force constants of Tables 2 and 3, we have calculated the frequencies of various isotopic species, and in Table 4 we compare these to the available experimental data.

DISCUSSION

As can be seen in Table 2, in all cases the dominant force constant is K_1, representing the valence bond, A-B, which is larger than the bending constant, δ, which in turn is larger than

TABLE 1

Fundamental Frequencies, Bond Angles and Atomic Masses of Non-Linear Triatomic (C_{2v}) Molecules

Molecule	Atomic Masses (u)		Bond* Angle 2α	Fundamental Frequencies+ (cm^{-1})		
	m_A	m_B		ω_1	ω_2	ω_3
H_2O	15.995	1.008	105°	3657	1595	3756
H_2S	32.064	1.008	92°	2615	1183	2626
H_2Se	78.96	1.008	90°	2345	1034	2358
SO_2	32.064	15.995	120°	1151	518	1362
NO_2	14.003	15.995	120°	1318	750	1618
O_3	15.995	15.995	127°	1103	701	1042
F_2O	15.995	18.998	104°	928	461	831
Cl_2O	15.995	35.453	111°	639	296	686

* From Ref. 9. • From Ref. 10.

TABLE 2

Force Constants for Non-Linear Triatomic (C_{2v}) Molecules

Molecule	Force Constants ($u\ cm^{-2}$)*		
	K_1	K_2	δ
H_2O	$1.3175x10^{7}$	$-2.80x10^{5}$	$1.304x10^{6}$
H_2S	$6.732x10^{6}$	$-4.60x10^{4}$	$7.07x10^{5}$
H_2Se	$5.534x10^{6}$	$-6.40x10^{4}$	$5.65x10^{5}$
SO_2	$1.6972x10^{7}$	$-6.52x10^{5}$	$1.596x10^{6}$
NO_2+	$1.4044x10^{7}$	$1.070x10^{6}$	$2.057x10^{6}$
O_3	$6.675x10^{6}$	$6.17x10^{5}$	$3.219x10^{6}$
F_2O	$5.301x10^{6}$	$-4.72x10^{5}$	$2.276x10^{6}$
Cl_2O	$4.160x10^{6}$	$1.62x10^{5}$	$8.95x10^{5}$

*Working units from $K = \mu\omega^2$ with μ in atomic mass units (u) and ω in wavenumbers (cm^{-1}). To convert to standard units multiply table entries by $5.90x10^{-5}$ for Nm^{-1} or by $5.90x10^{-2}$ for $dyn.cm^{-1}$.

+For NO_2, the observed value of ω_3 leads to complex force constants. The force constants in the table give the following frequencies: $\omega_1 = 1318$, $\omega_2 = 750$, $\omega_3 = 1592cm^{-1}$. (see text)

TABLE 3

Optimized Force Constants (K_1 and δ) and Calculated Frequencies For Non-Linear Triatomic (C_{2v}) Molecules.

Molecule	Force Constants(ucm^{-2}) K_1	δ	Calculated Frequencies(cm^{-1}) ω_1	ω_2	ω_3	%RMS* Deviation
H_2O	$1.308x10^7$	$1.172x10^6$	3687	1581	3742	0.73
H_2S	$6.729x10^6$	$6.805x10^5$	2623	1180	2625	0.23
H_2Se	$5.515x10^6$	$5.277x10^5$	2354	1025	2354	0.56
SO_2	$1.685x10^7$	$1.348x10^6$	1161	513	1357	0.78
NO_2	$1.535x10^7$	$2.463x10^6$	1342	730	1614	1.87
O_3	$6.771x10^6$	$3.651x10^6$	1162	655	1049	4.90
F_2O	$5.310x10^6$	$1.883x10^6$	885	489	832	4.41
Cl_2O	$4.149x10^6$	$9.875x10^5$	651	289	685	1.75

*Using observed frequencies in Table 1. See text for definition.

the non-bonded B-B interaction, K_2. In fact K_2 is so small (usually less than 0.1 K_1) for most molecules, that it may be neglected, and a satisfactory representation of the three fundamental frequencies may be obtained by optimizing the two parameters, K_1 and δ, as shown in Table 3. With this simplified model, only for ozone and oxygen difluoride is the RMS deviation greater than 2%. It is noted that both K_1 and δ show decreasing trends for the sequences $H_2O \rightarrow H_2S \rightarrow H_2Se$ and $F_2O \rightarrow Cl_2O$, as expected on chemical bonding grounds.

The small negative value for K_2 for most molecules is difficult to justify with electrostatic interactions between point charges on atomic centres, as discussed in an earlier paper[1]. However, a more complex charge distribution could lead

TABLE 4

Comparison of Calculated and Observed Frequencies (cm^{-1}) for Isotopic $AB_2(C_{2v})$ Molecules

Molecule	Observed Frequencies[□]			Calculated Frequencies[*]				Calculated Frequencies[+]			
	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	Δ%[x]	ω_1	ω_2	ω_3	Δ%[x]
D_2O	2671	1178	2788	2654	1163	2756	1.06	2668	1153	2742	1.55
H_2O^{18}	3650	1588	3742	3647	1589	3741	0.06	3677	1575	3727	0.68
D_2S	1696	855	1999	1881	850	1889	7.06	1882	846	1885	7.16
D_2Se	1739	754	1744	1669	735	1678	3.50	1675	732	1675	3.54
SO_2^{18}	1101	497	1318	1103	495	1318	0.26	1111	491	1313	0.52
$N^{15}O_2$	1306	740	1580	1296	745	1558	1.00	1319	729	1579	1.03
O_3^{18}	1038	660	974	1040	661	982	0.50	1095	618	989	4.93

[□] From Refs. 10 and 11.

[*] Using 3 force constants of Table 2.

[+] Using 2 force constants of Table 3.

[x] Percentage root mean square deviation (see text).

to this result. Because K_2 mostly affects the bending mode, putting it equal to zero, as in Table 3, is compensated by changes in δ rather than K_1. This is clear when values of K_1 in Tables 2 and 3 are compared. Only for NO_2 is the change substantial (~9%). This molecule is anomalous, in that solutions to equations (2) and (3) are very sensitive to mass, angle and frequency values, leading to complex results in some cases. The observed frequency values, in fact, lead to non-physical force constants. In Table 2, an optimized set of force constants reproduces the ω_1 and ω_2 frequencies exactly, but the calculated ω_3 is 26 cm^{-1} lower than the observed value, giving an RMS deviation of 0.9%, about half that of the two parameter model (Table 3).

For the two molecules with bond angle close to 90°, H_2S and H_2Se, it is found that the two stretching frequencies, ω_1 and ω_3, are almost degenerate. This has a simple explanation in terms of the model described in this paper. If $\alpha \approx 45^\circ$ and $m_B \ll m_A$, equation (1) reduces to $\omega_3 \approx (K_1/m_B)^{1/2}$. Similarly, equation (2) gives $\omega_1^2 + \omega_2^2 \approx (K_1 + 2\delta)/m_B$, if K_2 is neglected, and equation (3) becomes $\omega_1^2\omega_2^2 \approx 2K_1\delta/m_B^2$. These last two equations then simplify to give $\omega_1^2 \approx K_1/m_B$ and $\omega_2^2 \approx 2\delta/m_B$. Hence $\omega_1 \approx \omega_3$, as observed. Moreover, the bending mode, ω_2, is related to the stretching modes, ω_1 and ω_3, as follows: $\omega_2^2 = \omega_1^2 2\delta/K_1$. From Table 3 we see that $\delta/K_1 \approx 0.1$ and so we expect $\omega_2/\omega_1 \approx 0.45$. The experimental ratios of these frequencies are 0.45 for H_2S and 0.44 for H_2Se.

The agreement between experimental and calculated values of the isotopic frequencies, shown in Table 4, is quite acceptable, especially for the three parameter model. Only for the deuterated molecules, where anharmonic effects, neglected in this model, are different for the H and D species is the RMS deviation greater than 1%. This is especially true for D_2S, where Fermi resonance between ω_1 and $2\omega_2$ has perturbed the observed value of ω_1 from its harmonic value. Computations are in progress to obtain analytical expressions for the frequencies of non-linear ABC type molecules, a special case of these being partially deuterated species such as HDS. These will be reported in a later paper.

The most likely candidate of the molecules discussed in this paper for extension to lattice dynamics calculations is sulphur dioxide. This has an orthorhombic unit cell containing two molecules[12,13] and its vibrational spectra in both the lattice and internal mode regions are well documented[14]. Of the other molecules, some have complicated unit cells and several solid phases (H_2O, H_2S and H_2Se), one forms dimers in the crystal ($NO_2 \rightarrow N_2O_4$), and the crystal structure of the other (O_3) is unknown. Lattice dynamics calculations on SO_2 are in progress and will be the subject of a future paper.

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