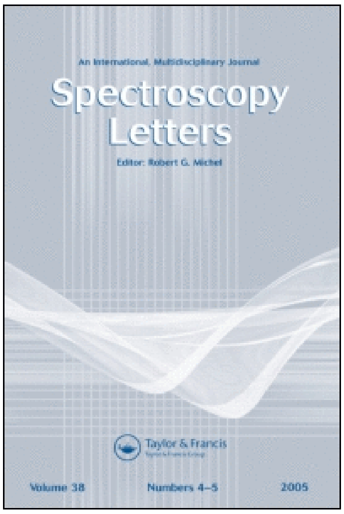

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Cartesian Dynamics of Simple Molecules V Non-Linear Triatomics (C_s Symmetry)

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CARTESIAN DYNAMICS OF SIMPLE MOLECULES
V NON-LINEAR TRIATOMICS (C_s SYMMETRY)

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

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ABSTRACT

A simple spring model for molecular vibrations is applied to non-linear triatomic ABC-type molecules with C_s point group. The development is in terms of Cartesian co-ordinates, which offers certain advantages for extensions to lattice dynamics calculations. Analytical expressions for the three normal mode frequencies are derived in terms of two stretching and one bending force constants. The model is applied to a number of ABC-type molecules and to asymmetric isotopic species of AB_2-type non-linear molecules. The validity of the model is demonstrated by the satisfactory agreement between calculated and observed frequencies of isotopic species. Examination of the calculated eigenvectors shows that mixing between the A-B and B-C stretches and ABC bend is appreciable. For DOCl a new value of the bending frequency is suggested.

INTRODUCTION

In previous papers in this series[1-4], a simple spring model for molecular vibrations was described and applied to diatomic, triatomic and quadratomic molecules. The method makes use of

Newton's laws and Hooke's law and is developed in terms of Cartesian rather than internal molecular coordinates. It offers certain advantages for extensions to lattice dynamics calculations of molecular crystals[5-9], such as the use of a uniform treatment of intra- and inter-molecular forces and the estimation of crystal field splittings of internal modes as well as the frequencies of lattice modes. In this paper, the model is applied to non-linear ABC type molecules, such as partially deuterated water, HDO, and the nitrosyl halides, XNO, where X is F, Cl or Br.

In the application of the method to non-linear triatomics of the AB_2 type[3], such as H_2O and SO_2, difficulties were experienced in calculating the various reactive forces involved during the normal vibrations, especially the bending mode, such that no net force or torque was applied to the molecule as a whole. These problems are compounded in the less symmetric molecules considered here. Consequently, we have adapted the method slightly, so that the potential energy is first expressed in terms of spring constants and internal coordinates (bond lengths and angles), which are then transformed to Cartesian coordinates. The development is then in terms of the Lagrangian formalism which is, of course, entirely equivalent to the Newtonian approach used earlier and has the advantage that difficulties concerning unbalanced forces and torques are avoided.

Analytical expressions are derived for the normal mode frequencies of these molecules in terms of stretching and bending

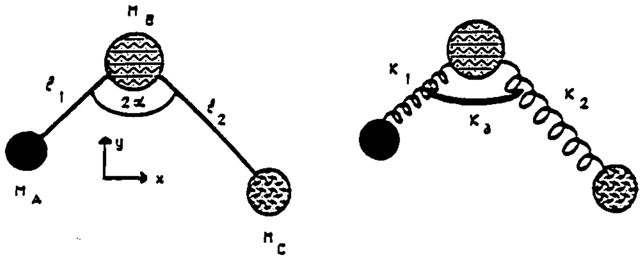

FIG. 1 Geometry and Spring Constant Model for ABC Non-Linear Molecules

(a)

force constants, atomic masses, bond lengths and bond angle, making use of MAPLE[10], an interactive symbolic computational technique developed at the University of Waterloo. Values for these force constants are obtained for a number of these ABC molecules by numerical approximation after substitution of the observed Raman and infrared frequencies into the equations. The form of the normal modes is verified by calculation of eigenvectors. It is also confirmed that the analytical expressions for the eigenfrequencies reduce to those expected for more symmetric molecules such as non-linear AB_2 and linear ABC types. The validity of the model is tested by comparing calculated and observed frequencies of various isotopic species.

The geometry of these ABC-type molecules, which have point group C_s is shown in Figure 1(a). Similarly to its AB_2-type counterparts there are 9 degrees of freedom, of which 3 correspond to pure translations and another 3 to pure rotations. There are thus 3 internal degrees of freedom, all involving motion in the plane of the molecule. There are two stretching modes and one bending mode, but because all modes are of the same species, mixing may occur, the extent of which being dependent on the geometry and values of the force constants. All modes are both Raman and infrared active. In principle, the three observed frequencies can be used to calculate three independent force constants.

DESCRIPTION OF THE MODEL

We introduce longitudinal springs K_1 and K_2 for the AB and BC bonds respectively and a bending spring K_δ, as shown in Figure 1(b). The potential energy is then expressed in terms of changes in bond lengths and bond angle as follows:

$$V = \frac{1}{2} K_1 (\Delta\ell_1)^2 + \frac{1}{2} K_2 (\Delta\ell_2)^2 + 2 K_\delta (\Delta\alpha)^2 \qquad (1)$$

Now $\ell_1^2 = \left(X_A - X_B\right)^2 + \left(Y_A - Y_B\right)^2$

$$\ell_2^2 = \left(X_C - X_B\right)^2 + \left(Y_C - Y_B\right)^2$$

and $\cos 2\alpha = \left(\ell_1^2 + \ell_2^2 - s^2\right)/2\ell_1\ell_2$

where $s^2 = \left(X_C - X_A\right)^2 + \left(Y_C - Y_A\right)^2$

By differentiation and use of relations such as $\left(X_A - X_B\right) = -\ell_1 \sin\alpha$, $\left(Y_A - Y_B\right) = -\ell_1 \cos\alpha$, etc., and $\Delta X_A = x_B$, etc., we obtain the following expressions for the displacements occurring in eqn. (1):

$$\Delta\ell_1 = \left(x_B - x_A\right)\sin\alpha + \left(y_B - y_A\right)\cos\alpha$$

$$\Delta\ell_2 = \left(x_C - x_B\right)\sin\alpha - \left(y_C - y_B\right)\cos\alpha$$

and $$\ell_1\ell_2\,\Delta\alpha = \left[-x_A\ell_2 + x_B\left(\ell_2 - \ell_1\right) + x_C\ell_1\right]\cos\alpha + \left[y_A\ell_2 - y_B\left(\ell_1 + \ell_2\right) + y_C\ell_1\right]\sin\alpha$$

The potential energy, V, is now in terms of the six Cartesian co-ordinates. It is straightforward to similarly express the kinetic energy, T, and hence form the Lagrangian L = T - V. Differentiation with respect to each of these variables then leads to the six coupled equations of motion, an example of which is given below:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_A}\right) - \frac{\partial L}{\partial x_A} = 0$$

or

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_A}\right) + \frac{\partial V}{\partial x_A} = 0$$

The resulting dynamical matrix in terms of Cartesian co-ordinates leads to a 6×6 secular determinant, which is shown in Table 1.

The expansion of this determinant and subsequent solution for the six matrix eigenvalues involve a considerable amount of tedious algebra, much of which can be circumvented with the use of MAPLE[10]. The final roots have the following form:

$$\omega_0 = \omega_0' = \omega_0'' = 0\,. \tag{2}$$

$$\omega_1^2 + \omega_2^2 + \omega_3^2 = K_1\left[\frac{1}{M_A} + \frac{1}{M_B}\right] + K_2\left[\frac{1}{M_C} + \frac{1}{M_B}\right] + K_\delta C \tag{3a}$$

$$\omega_1^2\omega_2^2 + \omega_1^2\omega_3^2 + \omega_2^2\omega_3^2 = K_1K_2\left[\frac{M_A + M_B + M_C}{M_AM_BM_C} + \frac{\sin^2 2\alpha}{M_B^2}\right] + K_1K_\delta\left[-\frac{\sin^2 2\alpha}{M_B^2\ell_1^2} + \left(\frac{1}{M_A} + \frac{1}{M_B}\right)C\right]$$

$$+ K_2K_\delta\left[-\frac{\sin^2 2\alpha}{M_B^2\ell_2^2} + \left(\frac{1}{M_C} + \frac{1}{M_B}\right)C\right] \qquad (3b)$$

$$\omega_1^2\omega_2^2\omega_3^2 = \frac{K_1K_2K_\delta\left(M_A+M_B+M_C\right)C}{M_AM_BM_C} \qquad (3c)$$

$$\text{where} \quad C = \left[\frac{\ell_1^2}{M_C} + \frac{\ell_2^2}{M_A} + \frac{\ell_1^2 + \ell_2^2 - 2\ell_1\ell_2\cos 2\alpha}{M_B}\right]\Big/\ell_1^2\ell_2^2$$

Equations (2) represent the three zero frequency modes corresponding to the two translational and one rotational in-plane modes. There are, of course, an additional three out-of-plane zero frequency modes (two rotations and one translation). Equations (3) are the three normal vibrational modes of A species. If we set $M_A = M_C = M$, $\ell_1 = \ell_2 = \ell$ and $K_1 = K_2 = K$, we obtain the equations given by Herzberg[11] for the valence force treatment of AB_2 molecules of C_{2V} symmetry. If we set $\alpha = 90°$, equations (3) reduce to those for non-centrosymmetric triatomic linear molecules ($C_{\infty V}$ symmetry), as derived in an earlier paper in this series[2]. In both these special cases, the equations factorize. For the C_{2V} molecules, the asymmetric stretch, ω_3, decouples from ω_1, the symmetric stretch, and ω_2 the bend, with the expressions for ω_1 and ω_2 remaining in the form of sum and product of roots. For the $C_{\infty V}$ molecules, the bending mode ω_3 decouples from the two stretching modes. For the general case of non-linear ABC-type molecules, the three force constants, K_1, K_2 and K_δ, can in principle be evaluated numerically from equations (3) after substitution of

TABLE 1

Secular Determinant for ABC Non-Linear Molecules

$$
\begin{array}{c|cccccc|}
 & X_A & X_B & X_C & Y_A & Y_B & Y_C \\
\hline
X_A & \begin{array}{l} M_A\omega^2-K_1\sin^2\alpha \\ -K_\delta\cos^2\alpha/\ell_1^2 \end{array} & \begin{array}{l} K_1\sin^2\alpha \\ +K_\delta(\ell_2-\ell_1)\cos^2\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} K_\delta\cos^2\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} -K_1\sin\alpha\cos\alpha \\ +K_\delta\sin\alpha\cos\alpha/\ell_1^2 \end{array} & \begin{array}{l} K_1\sin\alpha\cos\alpha \\ -K_\delta(\ell_1+\ell_2)\sin\alpha\cos\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} K_\delta\sin\alpha\cos\alpha/\ell_1\ell_2 \\ \end{array} \\
X_B & \begin{array}{l} K_1\sin^2\alpha \\ -K_\delta(\ell_1-\ell_2)\cos^2\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} M_B\omega^2-K_1\sin^2\alpha-K_2\sin^2\alpha \\ -K_\delta(\ell_2-\ell_1)^2\cos^2\alpha/\ell_1^2\ell_2^2 \end{array} & \begin{array}{l} K_2\sin^2\alpha \\ -K_\delta(\ell_2-\ell_1)\cos^2\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} K_1\sin\alpha\cos\alpha \\ -K_\delta(\ell_2-\ell_1)\cos\alpha\sin\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} -K_1\sin\alpha\cos\alpha+K_2\sin\alpha\cos\alpha \\ +K_\delta(\ell_2^2-\ell_1^2)\sin\alpha\cos\alpha/\ell_1^2\ell_2^2 \end{array} & \begin{array}{l} -K_2\sin\alpha\cos\alpha \\ -K_\delta(\ell_2-\ell_1)\sin\alpha\cos\alpha/\ell_1\ell_2^2 \end{array} \\
X_C & \begin{array}{l} K_\delta\cos^2\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} K_2\sin^2\alpha \\ -K_\delta(\ell_2-\ell_1)\cos^2\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} M_C\omega^2-K_2\sin^2\alpha \\ -K_\delta\cos^2\alpha/\ell_2^2 \end{array} & \begin{array}{l} -K_\delta\sin\alpha\cos\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} -K_2\sin\alpha\cos\alpha \\ +K_\delta(\ell_1+\ell_2)\sin\alpha\cos\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} +K_2\sin\alpha\cos\alpha \\ -K_\delta\sin\alpha\cos\alpha/\ell_2^2 \end{array} \\
Y_A & \begin{array}{l} -K_1\sin\alpha\cos\alpha \\ +K_\delta\sin\alpha\cos\alpha/\ell_1^2 \end{array} & \begin{array}{l} K_1\sin\alpha\cos\alpha \\ -K_\delta(\ell_2-\ell_1)\sin\alpha\cos\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} -K_\delta\sin\alpha\cos\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} M_A\omega^2-K_1\cos^2\alpha \\ -K_\delta\sin^2\alpha/\ell_1^2 \end{array} & \begin{array}{l} +K_1\cos^2\alpha \\ +K_\delta(\ell_1+\ell_2)\sin^2\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} -K_\delta\sin^2\alpha/\ell_1\ell_2 \\ \end{array} \\
Y_B & \begin{array}{l} K_1\sin\alpha\cos\alpha \\ -K_\delta(\ell_1+\ell_2)\sin\alpha\cos\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} -K_1\sin\alpha\cos\alpha+K_2\sin\alpha\cos\alpha \\ +K_\delta(\ell_2^2-\ell_1^2)\sin\alpha\cos\alpha/\ell_1^2\ell_2^2 \end{array} & \begin{array}{l} -K_2\sin\alpha\cos\alpha \\ +K_\delta(\ell_1+\ell_2)\sin\alpha\cos\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} +K_1\cos^2\alpha \\ +K_\delta(\ell_1+\ell_2)\sin^2\alpha/\ell_1^2\ell_2 \end{array} & \begin{array}{l} M_B\omega^2-K_1\cos^2\alpha-K_2\cos^2\alpha \\ -K_\delta(\ell_1+\ell_2)^2\sin^2\alpha/\ell_1^2\ell_2^2 \end{array} & \begin{array}{l} +K_2\cos^2\alpha \\ +K_\delta(\ell_1+\ell_2)\sin^2\alpha/\ell_1\ell_2^2 \end{array} \\
Y_C & \begin{array}{l} +K_\delta\sin\alpha\cos\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} -K_2\sin\alpha\cos\alpha \\ -K_\delta(\ell_2-\ell_1)\sin\alpha\cos\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} K_2\sin\alpha\cos\alpha \\ -K_\delta\sin\alpha\cos\alpha/\ell_2^2 \end{array} & \begin{array}{l} -K_\delta\sin^2\alpha/\ell_1\ell_2 \\ \end{array} & \begin{array}{l} +K_2\cos^2\alpha \\ +K_\delta(\ell_1+\ell_2)\sin^2\alpha/\ell_1\ell_2^2 \end{array} & \begin{array}{l} M_C\omega^2-K_2\cos^2\alpha \\ -K_\delta\sin^2\alpha/\ell_2^2 \end{array}
\end{array} = 0
$$

TABLE 2

Triatomic Asymmetric Molecules
Atomic Masses, Bond Lengths, Bond Angles and Observed Vibrational Frequencies*

Molecule	M_A (u)	M_B (u)	M_C (u)	ℓ_1 (Å)	ℓ_2 (Å)	2α (deg)	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})
FNO	18.9984	14.003	15.995	1.53	1.13	110.2	1876.8	775.5	522.9
ClNO	35.453	14.003	15.995	1.95	1.14	116.0	1835.6	336.4	603.2
BrNO	79.904	14.003	15.995	2.14	1.15	114.0	1822.3	269.2	548.0
HSiBr	1.008	28.0885	79.904	1.56	2.231	102.9	1548	408	774
HOCl	1.008	15.995	35.453	0.957	1.70	104	3626	739	1242
DOCl	2.014	15.995	35.453	0.957	1.70	104	2674	739	911

* From Refs. 12, 13.

the three fundamental vibrational frequencies observed spectroscopically.

RESULTS

The analytical solutions obtained above are applied to two distinct types of triatomic molecules. Firstly, a limited number of ABC non-linear molecules are considered. In Table 2, the atomic masses, bond lengths and angles, and observed vibrational frequencies of five such molecules are listed. Also included is data for DOCl, which will be discussed later. In Table 3, optimized values of the force constants K_1, K_2 and K_δ, derived from equations 3, are given. These force constants were then used to calculate the fundamental frequencies of various isotopic species, and these are compared with experimental values in Table 4. Secondly, asymmetric isotopes of AB_2^* non-linear molecules are

TABLE 3

Force Constants of Triatomic
Asymmetric ABC-type Molecules

Molecule	K_1 (ucm^{-2})	K_2 (ucm^{-2})	K_δ (urad^{-2})
FNO	$3.7320\text{x}10^6$	$2.7461\text{x}10^7$	$2.6332\text{x}10^6$
ClNO	$2.5980\text{x}10^6$	$3.3136\text{x}10^7$	$1.2375\text{x}10^6$
BrNO	$2.200\text{x}10^6$	$3.8846\text{x}10^7$	$9.5986\text{x}10^5$
HSiBr	$4.9735\text{x}10^7$	$5.8105\text{x}10^5$	$3.9318\text{x}10^5$
HOCl	$1.4467\text{x}10^8$	$1.4602\text{x}10^6$	$4.7553\text{x}10^5$
DOCl	$7.8344\text{x}10^7$	$1.4394\text{x}10^6$	$9.3126\text{x}10^5$

considered. In these, one of the B atoms is isotopically substituted, lowering the symmetry from C_{2V} to C_s, so that the equations derived earlier for C_{2V} triatomics[3] are no longer valid and must be replaced by equations 3 of the present paper. In table 5, we list the atomic masses, bond lengths and angle and vibrational frequencies of the parent molecules H_2O, H_2S and H_2Se and various isotopic species in which one hydrogen atom has been replaced with deuterium or tritium. Finally, in Table 6, the force constants derived from these frequencies using equations 3, (with $\ell_1 = \ell_2$) are listed.

DISCUSSION

The available data on ABC-type non-linear molecules is somewhat limited, with many uncertainties in both geometric and

TABLE 4

Frequencies of Isotopes of ABC-type Molecules

Isotope	Observed Frequencies[a] (cm^{-1})			Calculated Frequencies (cm^{-1})			ΔRMS (%)
	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	
$^{16}O^{15}NF$	1843.9	757.9	520.4	1843.8	757.6	520.1	0.05
$^{18}O^{14}NF$	1827.1	767.2	514.1	1878.9	772.6	496.5	2.59
$^{18}O^{15}NF$	1793.4	749.2	512.2	1841.2	754.9	495.1	2.48
$^{16}O^{15}NCl$	1803.6	588.8	334.3	1789.9	591.1	334.6	0.50
$^{18}O^{14}NCl$	----	595.5	329.3	1835.0	589.2	323.5	1.97
$^{18}O^{15}NCl$	1753.4	580.7	327.3	1789.9	576.9	322.2	1.55
$^{16}O^{15}NBr$	1800.3	----	266.8	1768.0	540.9	263.1	----
$^{18}O^{14}NBr$	1783.0	----	261.7	1768.0	538.3	252.4	----
$^{18}O^{15}NBr$	1749.9	527.1	259.6	1768.0	527.4	251.6	1.88
DOCl	2674	911	(739)[b]	2626.2	903.9	537.2	1.83

[a] From Ref. 13.

[b] Doubtful value (see text). ΔRMS is based on ω_1 and ω_2 only.

spectroscopic values. The molecules listed in Table 2 have been selected as having the most reliable data. For AB_2-type non-linear molecules[3], because of the equivalence of the two A-B bonds, we were able to introduce a weak spring between the two B atoms as one of the parameters. However, for many molecules this interaction was found to be negligible. For the ABC-type molecules discussed in the present paper, we already have three principle force constants, representing the A-B and B-C stretches and the ABC bend, and so we have neglected the weak interaction

TABLE 5

Asymmetric Isotopes of AB_2 Molecules

Atomic Masses, Bond Lengths, Bond Angles and Observed Vibrational Frequencies*

Molecule	M_A (u)	M_B (u)	M_C (u)	ℓ_1 (Å)	ℓ_2 (Å)	2α (deg)	ω_1	ω_2	ω_3
H_2O	1.008	15.995	1.008	0.957	0.957	104.5	3939	1648	3835
HOD	1.008	15.995	2.014	0.957	0.957	104.5	3889	1444	2823
HOT	1.008	15.995	3.020	0.957	0.957	104.5	3887	1370	2368
DOT	2.014	15.995	3.020	0.957	0.957	104.5	2833	1116	2359
H_2S	1.008	32.064	1.008	1.336	1.336	92.2	2733	1214	2721
HSD	1.008	32.064	2.014	1.336	1.336	92.2	2723	1058	1954
HST	1.008	32.064	3.020	1.336	1.336	92.2	2723	999	1619
DST	2.014	32.064	3.020	1.336	1.336	92.2	1951	796	1617
H_2Se	1.008	78.96	1.008	1.460	1.460	90.9	2439	1074	2453
HSeD	1.008	78.96	2.014	1.460	1.460	90.9	2443	919	1739
HSeT	1.008	78.96	3.020	1.460	1.460	90.9	2443	868	1430
DSeT	2.014	78.96	3.020	1.460	1.460	90.9	1739	690	1429

* From Ref. 13.

between the outer A and C atoms. If this were included, we would have an over-determined model with four parameters matching three frequencies, unless isotopic values were included.

Inspection of Table 3 shows that for the nitrosyl halides, the N-O bond, represented by K_2, is much stronger than the nitrogen-halogen bond, K_1. This is expected because of the much shorter N-O bond length, as shown in Table 2. (The value of K_2 for FNO is very close to that found for the N-O bond in nitrous oxide[2].) This, in turn, results from the covalent nature of the N-O bond[14], involving two electrons, whereas the nitrogen-halogen

TABLE 6

Force Constants of
Asymmetric Isotopes of AB_2-type Molecules

Molecule	k_1 (ucm^{-2})	k_2 (ucm^{-2})	k_α (urad^{-2})
H_2O(HOH)	1.460×10^7	1.460×10^7	1.106×10^6
HOD	1.459×10^7	1.459×10^7	1.063×10^6
HOT	1.459×10^7	1.452×10^7	1.101×10^6
DOT	1.457×10^7	1.458×10^7	1.068×10^6
H_2S(HSH)	6.969×10^6	6.969×10^6	1.620×10^5
HSD	6.948×10^6	6.948×10^6	1.617×10^5
HST	6.968×10^6	6.883×10^6	1.603×10^5
DST	6.964×10^6	6.963×10^6	1.617×10^5
H_2Se(HSeH)	5.900×10^6	5.900×10^6	1.295×10^5
HSeD	5.898×10^6	5.888×10^6	1.297×10^5
HSeT	5.896×10^6	5.878×10^6	1.295×10^5
DSeT	5.895×10^6	5.876×10^6	1.294×10^5

bond is mono-electronic. As the halogen atom increases in mass and size, the N-O bond strengthens, whereas both K_1 and K_δ weaken. The heavier halogens have larger electron clouds which repel the nitrogen electrons towards the electronegative oxygen and further increase K_2. On the other hand, the nitrogen-halogen separation increases, giving a broader potential well with less curvature and hence lower force constants for K_1 and K_δ.

Similar arguments are applicable to the HOCl molecule (and presumably to other halogenated molecules in this series, if reliable data were available), where the H-O bond (K_1) is much stronger than the O-Cl bond, again reflected in the differing bond lengths. However, the observed frequencies for DOCl lead to force constant values which are clearly not realistic from a physical standpoint. This is a consequence of the assumption that the bending mode frequency is unshifted upon deuteration[13] If we recalculate the DOCl frequencies using the HOCl force constants, we obtain the values listed in Table 4. These show good agreement for the stretching frequencies and suggest that the bending mode for DOCl is around 537 cm^{-1} rather than 739 cm^{-1} as assumed before. The agreement between calculated and observed frequencies for the other isotopic species listed in Table 4 is acceptable, considering the neglect of the interaction between the outer A-C atoms.

From Table 6, we see that the calculated force constants for the various isotopic species of H_2O, H_2S and H_2Se change very little from those of the parent molecules. This confirms the validity of the model and shows again that the neglect of the interaction between the end atoms is justified, especially for isotopic species of hydrogen. The small changes needed are more likely a consequence of the different anharmonicities experienced by the H, D and T atoms. The model described in this paper is, of course, strictly within the harmonic framework, and the force constants listed in Table 6 should be regarded as effective

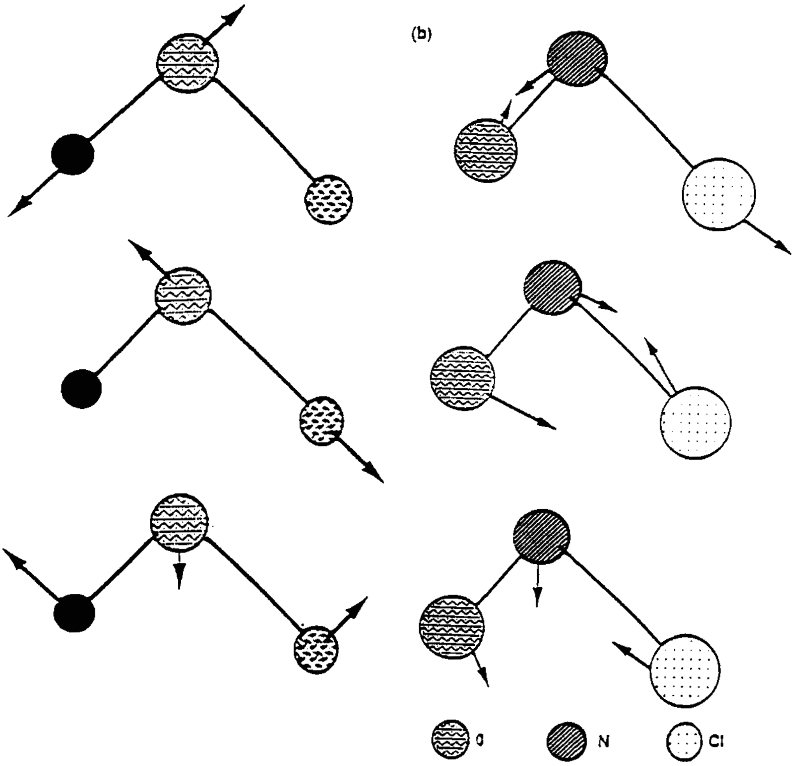

FIG. 2 (a) Unmixed Normal Modes of ABC Molecules. Top to Bottom: A-B stretch, B-C stretch, ABC bend. (b) Actual calculated eigenvectors for ClNO.

values, with the small changes compensating for the neglect of anharmonic contributions.

An examination of the eigenvectors of the three normal modes of all the molecules discussed in this paper shows that mixing between the A-B and B-C stretches and the ABC bend is present, as allowed by group theory, since all modes are of the same symmetry species. In some cases this mixing is appreciable, but it is still possible to describe the modes with the following approximate labels: ν_1, at the highest frequency, is predominantly the A-B stretch (with $M_A < M_C$) ν_2 at the intermediate frequency is mainly the B-C stretch, and ν_3 at the lowest frequency is the ABC bend. Eigenvectors for ClNO are shown in Figure 2. For the asymmetric isotopes considered in this report, the degree of mixing depends significantly on the masses involved. In other words, changing H to D or T affects not only the frequencies but the form of the eigenvectors.

Spectroscopic data on crystals of the molecules discussed in this paper is rather sparse, and consequently extension of the model to lattice dynamics calculations is not planned at the present time. In the next paper in this series, the application of the simple spring model to linear pentatomic molecules of the A_2B_3 type will be described.

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