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CARTESIAN DYNAMICS OF SIMPLE MOLECULES

VIII PLANAR QUADRATOMICS (D_{3h} SYMMETRY)

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

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ABSTRACT

The vibrations of planar A_3B type molecules with D_{3h} symmetry are analysed, by treating these molecules as a special case of A_2BC types with C_{2v} symmetry. Analytical expressions for the four normal mode frequencies are derived in terms of four force constants, and optimized values of the latter for the boron trihalides and sulphur trioxide are obtained and briefly discussed. Frequencies of various isotopic species are also calculated.

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INTRODUCTION

This is the eighth in a series of papers¹⁻⁷ in which a simple spring model for molecular vibrations is developed in terms of Cartesian co-ordinates. The model has been applied to various diatomic¹, triatomic^{1,2,3,5}, quadratomic^{4,7} and pentatomic⁶ molecules, and the approach has been shown to be equivalent to the conventional one which uses internal co-ordinates and intrinsically more suited for extensions to lattice dynamics calculations of molecular crystals⁸⁻¹⁴. In this report, the model is applied to planar quadratomic molecules of the A_3B type, such as the boron trihalides, which have D_{3h} symmetry.

Analytical expressions for the normal mode frequencies of these molecules are derived and compared with those of previous workers. The principal force constants are evaluated by substitution of the observed Raman and infrared frequencies, and these values are then used to obtain estimates of the frequencies of various isotopic species. Trends in the force constants for a series of halogenated molecules are briefly discussed.

The geometry for these molecules is shown in Figure 1(a) and may be compared with that of A_2BC molecules of C_{2v} symmetry, shown in Figure 1(b). There are 12 degrees of freedom, 3 corresponding to pure translations and another 3 to pure rotations about the centre of mass. A group theoretical analysis shows that the remaining 6 internal degrees of freedom comprise 2 non-degenerate modes (the symmetric stretch, ω_1 , belonging to A'_1 species and the out-of-plane bend, ω_2 , of A''_2 species) and 2 doubly-degenerate

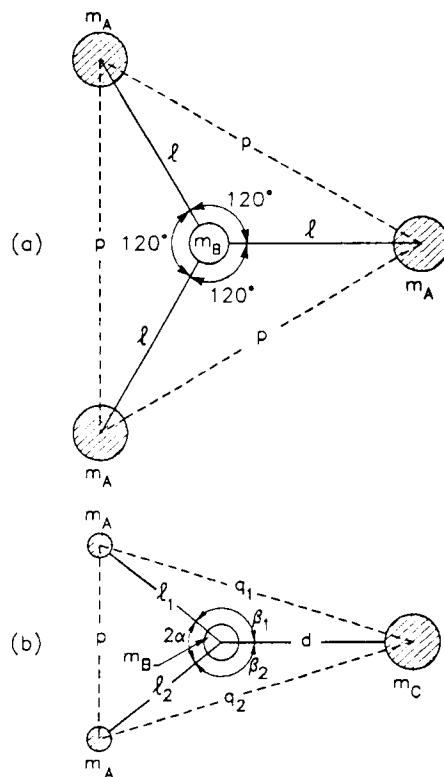


Figure 1 Geometries of (a) A_3B (D_{3h}) Molecules and (b) A_2BC (C_{2v}) Molecules.

modes, both of E' species (ω_3 , primarily the asymmetric stretch, and ω_4 , the in-plane asymmetric bend). The form of these normal modes is illustrated in Figure 2. The exact proportions of stretching and bending for ω_3 and ω_4 vary for different molecules and depend on the values of the force constants.

A correlation diagram showing the relationships between the modes for A_2BC (C_{2v}) and A_3B (D_{3h}) molecules is given in Figure 3.

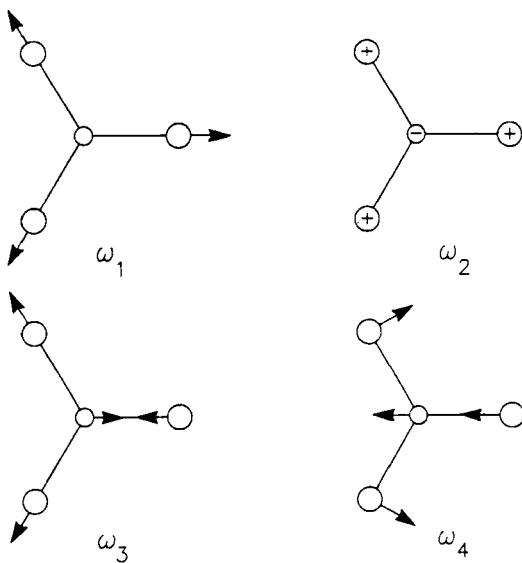


Figure 2 Approximate form of the Normal Modes of A_3B (D_{3h}) Molecules.

C_{2v}			D_{3h}		
<u>MODE</u>	<u>ACTIVITY</u>	<u>SPECIES</u>	<u>SPECIES</u>	<u>ACTIVITY</u>	<u>MODE</u>
ν_1, ν_2, ν_3, T_z	R,ir	A_1	A'_1	R	ν_1
R_z	R	A_2	A'_2	-	R_z
ν_4, ν_5, T_x, R_y	R,ir	A_2	E'	R,ir	ν_3, ν_4, T_{xy}
ν_6, T_y, R_z	R,ir	B_1	A''_1	-	-
		B_2	A''_2	ir	ν_2, T_z
			E''	R	R_{xy}

Figure 3 Correlation Diagram Relating the Normal Modes of A_2BC and A_3B Molecules.

in which the 3-fold (z) axis of the D_{3h} molecule corresponds to the y axis of the C_{2v} molecule. It may be seen that ω_2 and ω_3 of the C_{2v} molecule become the degenerate ω_3 of the D_{3h} molecule, and similarly, ω_4 and ω_5 coalesce to ω_4 . The out-of-plane bending mode ω_6 (B_2) of C_{2v} is relabelled ω_2 (A_2'') of D_{3h} . Whereas all modes of the A_2BC molecules are both Raman and infrared active, the higher symmetry of the A_3B molecules results in different selection rules: ω_1 is Raman active only, ω_2 is infrared active only, while ω_3 and ω_4 are active in both types of spectra.

DESCRIPTION OF THE MODEL

Rather than starting from first principles, as in earlier papers in this series¹⁻⁷, we choose here to treat the planar A_3B molecules as a special case of the A_2BC molecules discussed previously⁷. For a viable model, we require 4 force constants: these are the principal valence A-B stretching force constant K_1 , the weaker A-A stretching interaction K_2 , the A-B-A in-plane bending constant K_α , and the out-of-plane bending constant K_δ . These are shown in Figure 4(a) and may be related to the 7 force constants used for the A_2BC molecules shown in Figure 4(b). The identities involved in the transformation from A_2BC to A_3B molecules and the relationships between the two notations used are summarized in Table 1.

The rather complex analytical expressions for the frequencies of the A_2BC molecules were given in Table 2 of our previous paper⁷. When the above substitutions are made, some

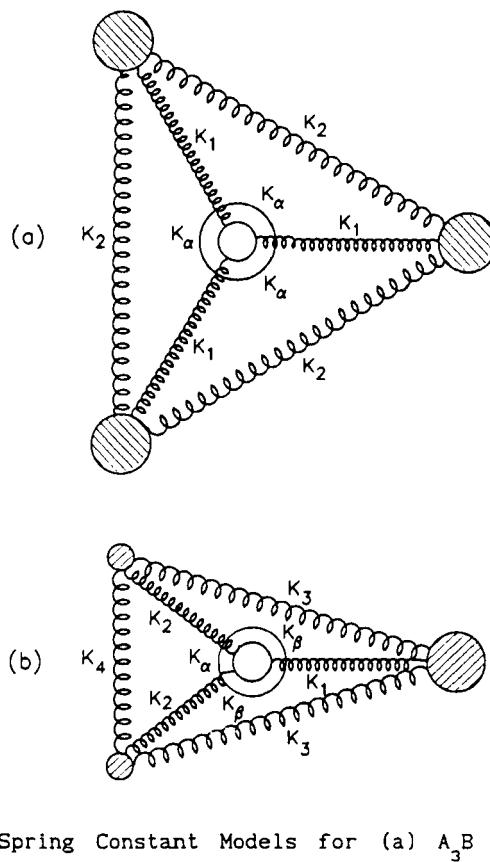


Figure 4 Spring Constant Models for (a) A_3 molecules and (b) A_2BC molecules. The out-of-plane bending constant K_γ is not shown.

drastic simplifications result. For example, the expressions for the $3 A_1$ modes, in terms of the coefficients of a cubic equation in ω^2 , factorize to give a separate equation for ω_1^2 , leaving ω_2^2 coupled to ω_3^2 in a quadratic equation. Moreover, this latter equation is identical to the one obtained for ω_4^2 and ω_5^2 , as required by the degeneracies discussed earlier. The final results

TABLE I

Relationships Between A_2^{BC} (C_{2v}) and A_3^B (D_{3h}) Molecules*

Identities for C_{2v} molecules	Values for D_{3h} molecules
$\ell_1 = \ell_2 = d$	ℓ
$q_1 = q_2 = p$	p
$2\alpha = \beta_1 = \beta_2$	120°
$b = d + \ell \cos \alpha$	$3\ell/2$
$a = \ell + d \cos \alpha$	$3\ell/2$
$q = (b^2 + \ell^2 \sin^2 \alpha)^{1/2}$	$\sqrt{3}\ell$
$m_A = m_C$	m_A
$K_1 = K_2$	K_1
$K_3 = K_4$	K_2
$K_\alpha = K_\beta$	K_α
$K_{\alpha\beta} = (2K_\alpha + K_\beta)/\ell^2$	$3K_\alpha/\ell^2$

*See Figures 1 and 4.

for the A_3^B normal mode frequencies are summarized in the following 4 equations:

$$\omega_1^2 = (K_1 + 3K_2)/m_A \quad (1)$$

$$\omega_2^2 = \frac{3K}{\ell^2} \left(\frac{1}{m_A} + \frac{3}{m_B} \right) \quad (2)$$

$$\omega_3^2 + \omega_4^2 = \left(K_1 + \frac{3K_\alpha}{\ell^2} \right) \left(\frac{1}{m_A} + \frac{3}{2m_B} \right) + \frac{3K_2}{2m_A} \quad (3)$$

$$\omega_3^2 \omega_4^2 = \left(\frac{3K_1 K_2}{4} + \frac{3K_\alpha}{4\ell^2} (4K_1 + 3K_2) \right) \left(\frac{1}{m_A^2} + \frac{3}{m_A m_B} \right) \quad (4)$$

We note first that if K_2 is put equal to zero, these equations reduce to those given by Herzberg¹⁵, once suitable changes in notation are made. In our earlier publication⁷, an error in one of Herzberg's equations for the frequencies of A_2BC molecules was pointed out. This is now confirmed, since this equation does not lead to his own result for A_3B molecules, when the identities listed in our Table 1 are substituted. The inadequacy of the 3-parameter model discussed by Herzberg may be

TABLE II

Fundamental Frequencies of Planar Quadratomic (D_{3h}) Molecules

<u>Molecule</u>	<u>State</u>	<u>Fundamental Frequencies (cm⁻¹)</u>				<u>Refs</u>
		<u>ω_1</u>	<u>ω_2</u>	<u>ω_3</u>	<u>ω_4</u>	
$B^{11}F_3$	gas	888	691	1449	480	16
$B^{11}Cl_3$	gas	471	460	954	255	17
$B^{11}Br_3$	liquid	279	372	816	151	18, 19
$B^{11}I_3$	solution	192	305	692	101	18, 19
SO_3	gas	1065	498	1391	530	16

seen in his table 44, where equations (1) and (4) above (with $K_2 = 0$) are used to find K_1 and K_α . The values of the left and right sides of his equation 211, corresponding to (3) above, are quite different. In fact, for some molecules, if equations (1) and (3) are used instead of (1) and (4) to find K_1 and K_α , the latter has a negative value, which is surely non-physical.

With 4 frequencies, we can use the above equations to solve for 4 force constants. We first use (2) to obtain K_γ , the out-of-plane bending constant. Then, with $K_2 = 0$, a starting value of K_1 is found from (1) and of K_α from (3), and a check for equality of the left and right sides of (4) is made. K_2 is then

TABLE III

Calculated Force Constants for Planar Quadratomic (D_{3h}) Molecules

<u>Molecule</u>	<u>Force Constants (u cm⁻²)*</u>			
	<u>K_1</u>	<u>K_2</u>	<u>K_α/ℓ^2</u>	<u>K_γ/ℓ^2</u>
$B^{11}F_3$	1.0266×10^7	1.572×10^6	4.71×10^5	4.895×10^5
$B^{11}Cl_3$	5.096×10^6	9.23×10^5	1.99×10^5	2.346×10^5
$B^{11}Br_3$	4.090×10^6	7.10×10^5	1.50×10^5	1.619×10^5
$B^{11}I_3$	3.068×10^6	5.37×10^5	9.37×10^4	1.106×10^5
SO_3	1.7007×10^7	3.80×10^5	9.81×10^5	5.297×10^5

*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 5.90×10^{-5} for Nm⁻¹ or by 5.90×10^{-2} for dyn. cm⁻¹.

systematically varied until (4) is indeed satisfied. As a final check, the optimized force constants are substituted, and the frequencies are calculated and compared with experimental values.

RESULTS

Fundamental frequencies of five quadratomic D_{3h} molecules are listed in Table 2. Force constants, calculated from equations (1) to (4), which reproduce all these frequencies are given in Table 3. A comparison of calculated and observed frequencies for various isotopic species is presented in Table 4. For the calculated values, the force constants of Table 3 have been used. Experimental data is sparse for the various chlorine and bromine isotopic species of the boron trihalides, but the calculated values are useful in the interpretation of the Raman and infrared spectra of crystals, where it is important to distinguish between crystal field and isotopic effects. It should be noted that equations (1) to (4) cannot be used directly for molecules with several halogen isotopes, such as $BCl_2^{35}Cl^{37}$, since the point group symmetry is changed for these (from D_{3h} to C_{2v}), and degeneracies are lost. The more general equations derived in our earlier paper on A_2BC molecules⁷ could be used. In general, the frequencies for these mixed isotopic molecules will be between those for the single isotopic types such BCl_3^{35} and BCl_3^{37} . Finally, it should be mentioned that we have attempted to model the frequencies of the quadratomic D_{3h} anions NO_3^- and CO_3^{2-} . Although sets of force constants which exactly reproduce the frequencies were found, they

TABLE IV

Comparison of Calculated and Observed Frequencies (cm⁻¹)
 for Isotopic Planar Quadratomic (D_{3h}) Molecules

<u>Molecule^x</u>	<u>Calculated Frequencies*</u>				<u>Observed Frequencies[†]</u>			
	<u>ω_1</u>	<u>ω_2</u>	<u>ω_3</u>	<u>ω_4</u>	<u>ω_1</u>	<u>ω_2</u>	<u>ω_3</u>	<u>ω_4</u>
B ¹⁰ F ₃	888.0	719.2	1502.0	482.1	888	719	1503	482
B ¹⁰ Cl ₃	471.0	480.3	993.5	255.8	471	480	994	255
B ¹⁰ Br ₃	279.0	389.4	852.9	151.2	279	390	856	151
B ¹⁰ I ₃	192.0	319.4	724.0	101.1	192	320	725	101
B ¹¹ Cl ₃ ³⁵	474.3	460.3	955.1	256.8				
B ¹¹ Cl ₃ ³⁷	461.3	459.2	951.1	250.1				
B ¹⁰ Cl ₃ ³⁵	474.3	480.6	994.5	257.4				
B ¹⁰ Cl ₃ ³⁷	461.3	479.5	990.7	250.8				
B ¹¹ Br ₃ ⁷⁹	280.7	372.2	816.4	151.9				no experimental
B ¹¹ Br ₃ ⁸¹	277.3	372.0	815.7	150.1				data available
B ¹⁰ Br ₃ ⁷⁹	280.7	389.5	853.2	152.1				
B ¹⁰ Br ₃ ⁸¹	277.3	389.3	852.5	150.3				
S ³² O ₃ ¹⁸	1004.1	487.2	1349.9	503.9				
S ³⁴ O ₃ ¹⁶	1065.2	489.6	1373.0	528.1				
S ³⁴ O ₃ ¹⁸	1004.1	478.2	1330.1	501.8				

^xWhere no superscript is given, the weighted mass corresponding to the natural isotopic abundances has been used.

* Using force constants of Table 3.

[†]From Refs. 16-19.

are considered to be non-physical. For example, K_2 and K_α/ℓ^2 have values which are larger than K_1 , the principal A-B stretching constant. For this reason these ions are not included in Tables 2 and 3. It appears that for these charged units, additional forces, associated with the presence of the cations, must be included in order to obtain a physically acceptable result.

DISCUSSION

It can be seen from Table 3 that the force constants calculated from this simple 4-parameter model all assume reasonable values. K_1 the valence A-B bond is dominant, with K_2 , representing the non-bonded A-A interaction, always much smaller. The bending constants, K_α and K_γ , are reasonably similar to each other for the boron trihalides, while the in-plane constant, K_α , is almost twice as large as the out-of-plane constant, K_γ , for SO_3 . As usual, the bending constants are much smaller than the principal stretching constants. The physical validity of the model is confirmed by the excellent agreement obtained for the frequencies of isotopic species, as shown in Table 4. For molecules where isotopic frequencies have not been observed, the predicted values in Table 4 may be used with some confidence. In an earlier paper from this laboratory²⁰, certain features in the Raman and infrared spectra of the solid boron trihalides were assigned to isotopic species, and these assignments are now confirmed from the splittings calculated for the isolated molecules.

For the boron trihalides, all four force constants show systematic decreases as the halogen mass increases, consistent with the larger interatomic separations involved. For example, in going from BF_3 to BI_3 , K_1 is decreased by a factor of 0.30, K_2 by 0.34, K_α/ℓ^2 by 0.20 and K_γ/ℓ^2 by 0.23. The sulphur trioxide molecule is characterized by a very strong S-O valence bond, K_1 , a strong in-plane bending constant K_α , and relatively weak O-O interactions (K_2).

The crystal structures of BCl_3 , BBr_3 and BI_3 have been determined and are isomorphic, with two molecules in a hexagonal unit cell²¹⁻²⁵, whereas that of BF_3 is unknown, but thought to be more complex, on the basis of its solid state spectra²⁶. The Raman and infrared spectra of crystalline BCl_3 , BBr_3 and BI_3 have been recorded²⁰, and so these systems are excellent candidates for an extension of the model described here to lattice dynamics calculations. This work is in progress in our laboratory and will be reported in a later paper.

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