143. *Normal Co-ordinate Analysis for* trans-*Centrosymmetric* X_2Y_2 *Molecules: Application to the Hyponitrite Ion.*

By D. J. MILLEN, C. N. POLYDOROPOULOS, and D. WATSON.

A normal co-ordinate treatment using a valence-force potential function has been made for *trans*-centrosymmetric X_2Y_2 molecules. The infrared and Raman spectra of the hyponitrite ion are reported and frequencies assigned in accord with the normal co-ordinate treatment. Force constants have been evaluated and an empirical correlation has been made of stretching force constants for a series of oxides and oxy-ions of nitrogen.

THE normal vibrational analyses of linear and *cis*-X_2Y_2 molecules of point groups $D_{\infty h}$ and C_{2v} are well known. The present paper provides an analysis for *trans*-centrosymmetric X_2Y_2 molecules belonging to the point group C_{2h}. The equations have been applied to the infrared and Raman spectra of the hyponitrite ion, $N_2O_2^{2-}$. The six normal vibrations fall into the following classes: 3 of species A_g, 2 of species B_u, and 1 of species A_u. A suitable set of symmetry co-ordinates which allows the factorization of the vibrational secular determinant into three blocks, corresponding to these classes is shown in Fig. 1. The displacement co-ordinates given in the Figure have been chosen so that there is no resultant moment, or translation of the centre of mass.

The kinetic and potential energies are given by:

$$2V = \sum_{ij} c_{ij}S_iS_j \quad \text{and} \quad 2T = \sum_{ij} d_{ij}\dot{S}_i\dot{S}_j$$

in which the coefficients of cross terms between symmetry co-ordinates of different classes are zero. The remaining d_{ij} were obtained by transformation of the symmetry co-ordinates to Cartesian displacement co-ordinates and comparison of coefficients with $2T = \sum m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$. The potential function used was the simple valence force one,

$$V = k_1(\Delta r_3^2) + k_2(\Delta r_1^2 + \Delta r_2^2) + k_\alpha(\Delta\alpha_1^2 + \Delta\alpha_2^2) + k_\beta(\Delta\beta_1^2 - \Delta\beta_2^2)$$

k_1 and k_2 are the stretching force constants of the N–N and N–O bonds, and k_α and k_β are the in- and out-of-plane bending force constants. By using the transformation $q_t = \sum_{k=1}^{t} l_{tk} S_k$, the c_{ij} were found in terms of the force constants.

The characteristic vibration frequencies ν can be obtained by solving the secular determinant $|c - \lambda d|$ for $\lambda = 4\pi\nu^2$. This may be done numerically. Alternatively, algebraic solution of the secular determinant yields the following expressions:

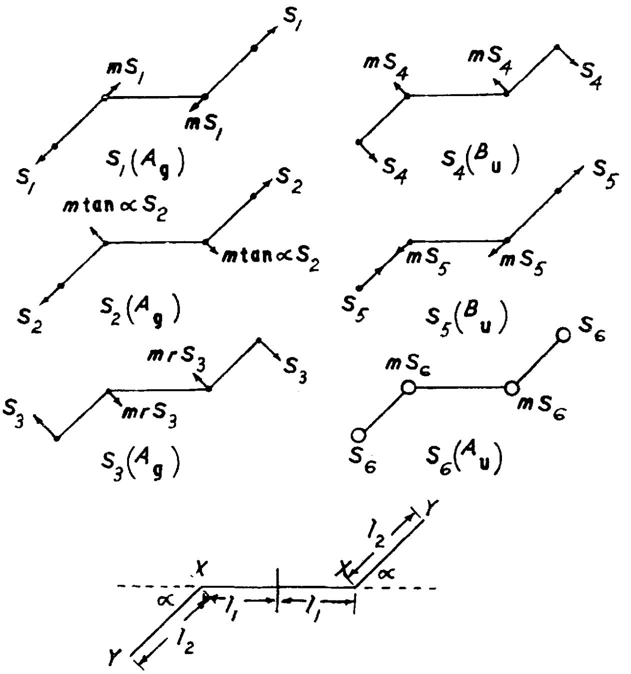


FIG. 1. *Symmetry co-ordinates.* $m = M_x/M_y$; $r = 1 + (l_2/l_1) \cos \alpha$.

$$\lambda_1\lambda_2\lambda_3 = \frac{2mM}{M_Y^3} \cdot \frac{k_1k_2k_\alpha}{l_2^2}$$

$$\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3 = \frac{2m^2(m \sin^2\alpha + 1)}{M_y^2} k_1k_2 + \frac{2m(mr^2 \cos^2\alpha + 1)}{M_y^2} \frac{k_1k_\alpha}{l_2^2} + \frac{(m + 1)M - m^2(r - 1)^2 \cos^2\alpha \sin^2\alpha}{M_y^2} \cdot \frac{k_2k_\alpha}{l_2^2}$$

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{2mk_1}{M_y} + \frac{(m + 1)k_2}{M_y} + \frac{M}{M_y} \cdot \frac{k_\alpha}{l_2^2}$$

$$\lambda_4 = \frac{k_\alpha}{l_2^2}\left(\frac{1}{M_x} + \frac{1}{M_y}\right)$$

$$\lambda_5 = k_2\left(\frac{1}{M_x} + \frac{1}{M_y}\right)$$

$$\lambda_6 = \frac{k_\beta}{l_2^2}\left(\frac{1}{M_x} + \frac{1}{M_y}\right)$$

In these expressions $M = mr^2 \cos^2 \alpha + m \sin^2 \alpha + 1$, $r = 1 + l_2/l_1 \cos \alpha$ and $m = M_y/M_x$, the ratio of the masses involved.

The Infrared and Raman Spectra of the Hyponitrite Ion.—The vibrational frequencies, observed for the hyponitrite ion by using mulls of the sodium salt for the infrared spectra and aqueous solutions for the Raman spectra, are given in the Table. The lines in the infrared spectra were reproducible from different samples, the only other lines present being attributable to small amounts of carbonate ion present as impurity. A slight complication arose in the case of the line at 863 cm.$^{-1}$. This falls between two maxima at 879 and 851 cm.$^{-1}$ due to the carbonate ion, but its frequency is unlikely to be in error by more than a few wave numbers. The frequencies are in reasonably good agreement with those reported by Kuhn and Lippincott,[1] except for the weaker line in the Raman spectrum, which they report at 958 cm.$^{-1}$. Instead we find a weak line at 1115 cm.$^{-1}$. The observation of good Raman spectra is made difficult by the continuous appearance of small gas bubbles in the solution, due to decomposition, but the appearance of the line at 1115 cm.$^{-1}$ in a spectrum excited by Hg λ 4047 Å is clearly shown in Fig. 2. Its existence was confirmed by its observation in spectra excited by Hg λ 4358 Å.

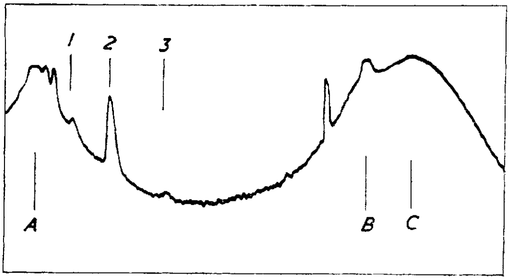


FIG. 2. *Raman spectrum of the hyponitrite ion. (The Raman frequency* 1383 *cm.*$^{-1}$ *occurs twice, excited strongly by* Hg λ 4047 Å *and weakly by* Hg λ 4078 Å.)

A, Hg λ 4358 Å. *B*, Hg λ 4078 Å. *C*, Hg λ 4047 Å.

1, 1383 cm.$^{-1}$. 2, 1383 cm.$^{-1}$. 3, 1115 cm.$^{-1}$.

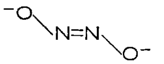
A preliminary investigation[2] appeared to show that the hyponitrite ion in Nujol mulls and potassium bromide discs exhibited different infrared spectra. Further work has shown the apparent difference arises in the following way. The hyponitrite ion spectrum in potassium bromide discs is complicated by the spectrum of the carbonate ion, which is present as impurity. The carbonate content of a sample in a disc is greater than that in a mull, presumably owing to conversion of hyponitrite into carbonate by atmospheric carbon dioxide during grinding. A further complication arises as there appears to be a change in the relative intensities of the carbonate ion bands. Such changes in relative intensities in potassium bromide discs have been reported previously.[3] If these factors are taken into account the spectra of discs accord with those of mulls.

Possible structures for the hyponitrite ion include (I—IV). It is evident from qualitative considerations that the spectra are not those to be expected for structure (III) or (IV). Six fundamentals are allowed in the Raman spectrum for (III) and five for (IV), whereas only two are observed. Similarly, for a staggered structure intermediate between (II) and (III), six fundamentals are allowed in the Raman spectrum. Again, for structures (III) and (IV) the selection rules allow five fundamental frequencies common to infrared and Raman spectra. Only one line is observed which could possibly be

$^-O{-}N{=}N{-}O^-$

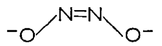
$D_{\infty h}$

(I)



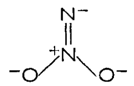
C_{2h}

(II)



C_{2v}

(III)



C_{2v}

(IV)

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[1] Kuhn and Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 1820.

[2] Millen, Polydoropoulos, and Watson, *Proc. Chem. Soc.*, 1957, 18.

[3] Wiberley, Sprague, and Campbell, *Analyt. Chem.*, 1957, **29**, 210.

regarded as common to both spectra, and so structures (III) and (IV) could be accommodated only if it happened that several allowed lines were too weak to be observed in the Raman effect. The appearance of the spectra points in fact to a structure with a centre of symmetry. Of the two possibilities (I) and (II), the former is unlikely on valency considerations. There is also spectroscopic evidence against it. If this were the structure of the ion, the frequencies in the Raman spectrum at 1383 and 1115 cm.$^{-1}$ would be attributed to $\sum_g^+$ stretching vibrations. The assumption of a simple valence force potential function leads to stretching force constants of 12·5 md/Å, and 0·7 md/Å for the N–N and N–O bonds respectively. Only an approximate description of the molecular force field can be expected from the assumption; nevertheless the value of 0·7 md/Å is unreasonably low for a N–O stretching force constant. It is not even possible to obtain a consistent interpretation of the spectrum on this basis. The N–O stretching force constant should also be obtainable directly from the infrared active $\sum_u^+$ stretching vibration. The appropriate frequency is obviously 1020 cm.$^{-1}$, which is the strongest band in the infrared spectrum, but of rather too high a frequency to be the infrared active π_u bending vibration. This yields the quite different value of 4·6 md/Å.

There remains the *trans*-structure (II) to be considered, and it will be shown that the spectra can be well understood in terms of this structure. In the infrared spectrum one B_u fundamental stretching frequency ν_5 and two bending fundamentals (ν_4, B_u, and ν_6, A_u) are to be expected. The strongest line in the spectrum at 1020 cm.$^{-1}$ is assigned as ν_5, for it is too high a frequency to be assigned as a bending vibration. This gives directly a value for k_2 of 4·6 md/Å. The two Raman frequencies are clearly to be assigned as two of the three A_g vibrations. Again, on account of their high values they are both assigned to stretching vibrations, the higher at 1383 cm.$^{-1}$ to ν_1, involving mainly –N=N– double-bond stretching and that at 1115 cm.$^{-1}$ to ν_2, essentially in-phase N–O bond stretching. There remain two more in-plane vibrations, ν_3 and ν_4, to be assigned. Of these ν_3 is presumably allowed so weakly in the Raman spectrum that it has not been observed. For the infrared active vibration ν_4, either of 863 or 504 cm.$^{-1}$ is a possible choice. However, it appears likely that neither of these is to be assigned as ν_4. The former leads to a $\angle$NNO deformation force constant of 3·3 md/Å, and the latter to 1·1 md/Å, both of which are high by comparison with similar force constants. This suggests that ν_4 falls below 400 cm.$^{-1}$ and has not been observed. The sixth normal vibration is the infrared-active out-of-plane bending mode. The only low-lying frequency observed in the infrared spectrum at 504 cm.$^{-1}$ is probably to be assigned as ν_6. This leads to $k_\beta/l_2^2 = 1·1$ md/Å, which falls well into the range observed for similar bending force constants.

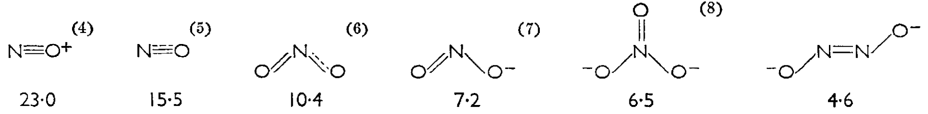
The assignments and force constants are collected in the Table. Approximate values have been estimated for the two unobserved fundamentals and assignments of combination frequencies have also been suggested. The values have been calculated for the structural parameters $r_{\text{N–N}} = 1·25$ Å, $r_{\text{N–O}} = 1·41$ Å, and $\alpha = 60°$.

Assignments and force constants.

2207	w	Infrared	$\nu_2 + \nu_5$	B_u	863	w	Infrared	$\nu_3 + \nu_4$	B_u
1383	s	Raman	ν_1	A_g	504	w	Infrared	ν_6	A_u
1129	w	Infrared	$2\nu_4 + \nu_6$	A_u	(485)	approx. calc.		ν_3	A_g
1115	w	Raman	ν_2	A_g	(370)	approx. calc.		ν_4	B_u
1020	s	Infrared	ν_5	B_u					

$k_1 = 6·9$ md/Å $\quad k_2 = 4·6$ md/Å $\quad k\alpha/l_2^2 = 0·6$ md/Å $\quad k\beta/l_2^2 = 1·1$ md/Å

The oxides and oxy-ions of nitrogen provide a good series of molecules in which to examine changes in force constants over a wide variation in bonding. The stretching force constants in md/Å are as follows:



For the polyatomic molecules the values have been evaluated from a valence force potential function including interaction cross-terms, except for the hyponitrite where there is at present insufficient spectroscopic information to allow these to be included. The force constants decrease uniformly with decreasing double-bond character. An approximately quantitative empirical relation is observed between force constant and bond order, if in each case the resonance structure written above is regarded as the important one and bond order taken as the average number of bonding electrons per bond. The nitronium ion is an exception, its stretching force constant being 17·3 md/Å, considerably greater than indicated for a double bond. This may be due to a stronger σ-bond formed in this case from nitrogen *sp*-hybridised atomic orbitals. The oxide N_2O_2 which is thought to be present in solid nitric oxide has not been included because its vibrational spectrum has not been analysed with certainty. It has been suggested [9] that the N-O asymmetric stretching frequency falls at 1700 cm.$^{-1}$; if this is correct, correlation with other molecules given here indicates that the N-O bonds are appreciably stronger than double bonds.

Experimental.—Sodium hyponitrite was prepared by reduction of sodium nitrite by sodium amalgam, followed by crystallisation from alkaline solutions.[10] The Raman spectra were observed by using a truncated-cone cell which just filled the aperture-cone of the spectrograph and allowed escape of gas bubbles formed by decomposition of the sample. The Raman spectra were recorded on a Hilger E 612 spectrograph, and infrared spectra on a Hilger D 209 spectrometer.

We are indebted to Dr. I. R. Beattie for valuable discussion about the spectra in potassium bromide discs, and to the State Scholarships Foundation, Athens, for an award to one of us (C. P.).

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

[*Received, August 5th*, 1959.]

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