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Vibrational Mean-Square Amplitude Matrices

V. Treatment of Bent Symmetrical XY_2 Molecules with Application to Nitrogen Dioxide

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The theory of mean-square amplitude matrices is applied to the bent symmetrical XY_2 molecular model. Numerical computations for nitrogen dioxide are reported, including the calculation of ten mean-square amplitude quantities for $^{14}NO_2$ and for $^{15}NO_2$, both at the temperatures $T = 0$ and 298 °K. An application of the isotope rule for mean-square amplitude matrix elements is also given.

Spectroscopical studies of bent symmetrical XY_2 molecules have been the subject of many publications (see, *e.g.* Refs.[1-6]). In the present article, some of the theoretical results for this type of molecules will be summarized and supplied with the study of the mean-square amplitude matrix. Numerical calculations for nitrogen dioxide will be reported.

THEORETICAL TREATMENT

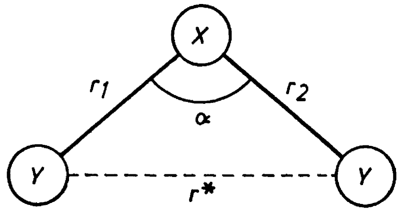
The harmonic vibrations of the considered molecular model are described by three internal coordinates, which may be chosen as a set of valence force coordinates (see Fig. 1). The following symmetry coordinates have been formed as normalized linear combinations of the valence force coordinates.

Symmetry species A_1: $\begin{cases} S_1 = (1/\sqrt{2})(r_1 + r_2) \\ S_2 = R\alpha \end{cases}$

Symmetry species B_1: $S_3 = (1/\sqrt{2})(r_1 - r_2)$

For the notations applied, see Fig. 1. It should be noticed that the angle displacement coordinate α is multiplied by R, designating the equilibrium X—Y distance.

Fig. 1. Notation used for the bent symmetrical XY_2 molecular model. The symbols denote deviations from the equilibrium values.



The potential energy matrix in terms of the given symmetry coordinates may be written

$$F = \begin{bmatrix} F_1 & F_{12} & 0 \\ & F_2 & 0 \\ (\text{symm.}) & & F_3 \end{bmatrix}$$

where

$$F_1 = k + k', \qquad F_2 = f, \qquad F_{12} = \sqrt{2}\, g, \qquad F_3 = k-k' \tag{1}$$

The potential energy function (V) in terms of the valence force coordinates will be written down, in order to explain the symbols used in eqn (1).

$$V = \tfrac{1}{2}[k(r_1^2 + r_2^2) + 2k'r_1r_2 + fR^2\alpha^2 + 2Rg(r_1 + r_2)\alpha] \tag{2}$$

The inverse kinetic energy matrix (G matrix) will not be given here. References are made to [7–10].

The symmetrized mean-square amplitude matrix [11,12] is given by

$$\Sigma = \begin{bmatrix} \Sigma_1 & \Sigma_{12} & 0 \\ & \Sigma_2 & 0 \\ (\text{symm.}) & & \Sigma_3 \end{bmatrix}$$

where

$$\Sigma_1 = \sigma + \sigma', \qquad \Sigma_2 = \tau, \qquad \Sigma_{12} = \sqrt{2}\, \varrho, \qquad \Sigma_3 = \sigma-\sigma' \tag{3}$$

The symbols introduced here are defind by:

$$\sigma = \overline{r_1^2} = \overline{r_2^2}, \qquad \sigma' = \overline{r_1r_2}, \qquad \tau = R^2\, \overline{\alpha^2}$$
$$\varrho = R\, \overline{r_1\alpha} = R\, \overline{r_2\alpha} \tag{4}$$

The following equations exist for the vibrational normal frequencies ($\lambda_k = 4\pi^2\nu_k^2$).

$$\lambda_1 + \lambda_2 = F_1(2\mu_X\cos^2A + \mu_Y) + 2F_2(2\mu_X\sin^2A + \mu_Y)$$
$$2\sqrt{2}\; F_{12}\mu_X\sin 2A \tag{5}$$

$$\lambda_1\lambda_2 = 2(F_1F_2-F_{12}^2)(2\mu_X+\mu_Y)\mu_Y \tag{6}$$

$$\lambda_3 = F_3(2\mu_X\sin^2A + \mu_Y) \tag{7}$$

Here μ_X and μ_Y denote the inverse masses of the X and Y atoms, respectively. The equilibrium value of the inter-bond angle is denoted by $2A$. Another set of equations, containing the mean-square amplitude quantities instead of the force constants, has been evaluated as given below. The values of Δ are connected with the normal frequencies by $\Delta_k = (h/8\pi^2\nu_k)\coth(h\nu_k/2kT)$, where h is Plack's constant, k Boltzmann's constant, and T the absolute temperature.

$$\begin{aligned}\Delta_1 + \Delta_2 = [&\Sigma_1(2\mu_X\sin^2A + \mu_Y) + \tfrac{1}{2}\Sigma_2(2\mu_X\cos^2A + \mu_Y) \\ &+ \sqrt{2}\Sigma_{12}\mu_X\sin2A](2\mu_X + \mu_Y)^{-1}\mu_Y^{-1}\end{aligned} \tag{8}$$

$$\Delta_1 \Delta_2 = \tfrac{1}{2}(\Sigma_1\Sigma_2 - \Sigma_{12}^2)(2\mu_X + \mu_Y)^{-1}\mu_Y^{-1} \tag{9}$$

$$\Delta_3 = \Sigma_3(2\mu_X\sin^2A + \mu_Y)^{-1} \tag{10}$$

Additional mean-square amplitude quantities are to be taken into acconut when the non-bonded Y...Y distance is considered. If the corresponding distance deviations are identified by the symbol r *, the following mean-square amplitude quantities are defined.

$$\tau^* = \overline{(r^*)^2}, \qquad \varrho^* = \overline{r_1r^*} = \overline{r_2r^*} \tag{11}$$

These quantities may be expressed in terms of those given by eqn (4) with the following result, deduced from geometrical considerations.

$$\begin{aligned}\tau^* &= 2(\sigma + \sigma')\sin^2A + \tau\cos^2A + 2\varrho\sin2A \\ \varrho^* &= (\sigma + \sigma')\sin A + \varrho\cos A\end{aligned} \tag{12}$$

NUMERICAL COMPUTATIONS

Normal frequencies. The normal frequencies [13] applied in the present calculations are shown in Table 1. It should be pointed out that the three frequencies of a specific bent symmetrical XY_2 molecule, say $^{14}NO_2$, are not sufficient for the complete determination of the harmonic vibrational constants.

Table 1. Experimental vibrational frequencies of nitrogen dioxide molecules.

Species	No.	Normal frequencies in cm^{-1} units [a] $^{14}NO_2$	$^{15}NO_2$
	1	1 357.8 [b]	1 343.3 [b]
A_1	2	756.8	747.1
B_1	3	1 665.5	1 628.6

[a] From Ref. [13]; all values are corrected for anharmonicity. The frequencies of $^{15}NO_2$ were revised to fit accurately the product rule with the physical constants here applied, the discrepancies from the values in the cited paper being insignificant.

[b] Based on estimated fundamentals from vibrational analysis.

Table 2. Calculated force constants for nitrogen dioxide.

Symbol	mdyne/Å	Symbol	mdyne/Å
F_1	12.8754	k	10.8840
F_2	1.1290	k'	1.9914
F_{12}	0.51315	f	1.1290
F_3	8.8927	g	0.36285

The value of $2A = 134° 15'$ for the valence angle, quoted in Ref. [13], has also been adopted in the present work.

Force constants. The normal frequency 1 665.5 cm^{-1} (see Table 1) gives the value $F_3 = 8.8927$ mdyne/Å without ambiguity for the force constant of the species B_1. The force constants of the species A_1, *viz.* F_1, F_2 and F_{12}, are going to be discussed in the following. To obtain real values of the force constants consistent with a set of normal frequencies, only limited ranges of the constants are allowed. With the normal frequencies of $^{14}NO_2$ given in Table 1, it is found from eqns (5), (6) for the interaction constant F_{12} in mdyne/Å

$$-0.55788 \leq F_{12} \leq 4.5686$$

All the possible values of the force constants here considered have been represented graphically by an ellipse, this being a usual procedure (*see, e.g.* Refs [3,5,6,14-18]). The stippled curve (see Fig. 2) represents one of the alternative solutions for the force constants, arising from the quadratic secular equation.

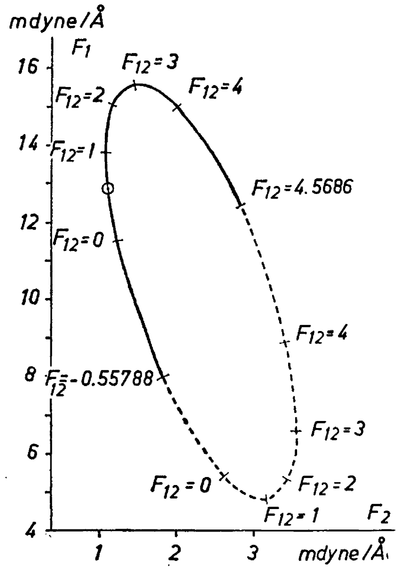


Fig. 2. Values of force constants for NO_2, consistent with $\omega_1 = 1357.8$ and $\omega_2 = 756.8$ cm^{-1}. ⊙ indicates the best calculated values (see the text).

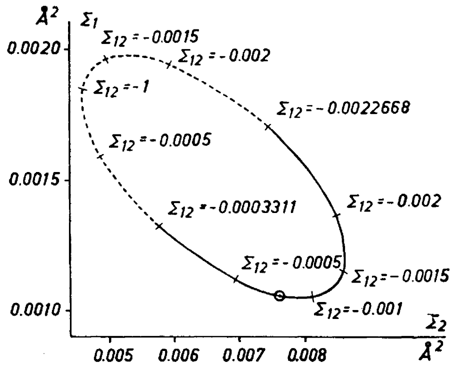


Fig. 3. Values of mean-square amplitude matrix elements at 298 °K for $^{14}NO_2$, consistent with $\omega_1 = 1357.8$ and $\omega_2 = 756.8$ cm^{-1}. ⊙ indicates the best calculated values (see the text).

With the additional knowledge of the normal frequencies of the $^{15}NO_2$ molecule, it is possible to calculate definite values of the force constants. The result of these calculations is given in Table 2, and the values of F_1 and F_2 in particular, are indicated on the curve of Fig. 2.

Mean-square amplitude quantities. An analogous procedure to that of the preceding paragraph is applied to the mean-square amplitude quantities of $^{14}NO_2$ at 298 °K. Eqn (10) gives the value 0.0018612 Å^2 for Σ_3. From eqns (8), (9), the remaining three mean-square amplitude matrix elements have been calculated and represented graphically in Fig. 3. The range for the interaction mean-quare amplitude in Å^2 is found to be

$$-0.0022668 \leq \Sigma_{12} \leq -0.0003311$$

The mean-square amplitudes of vibration of the two types of interatomic distances, *viz.* σ and τ^* in the present notation, are the most important ones.

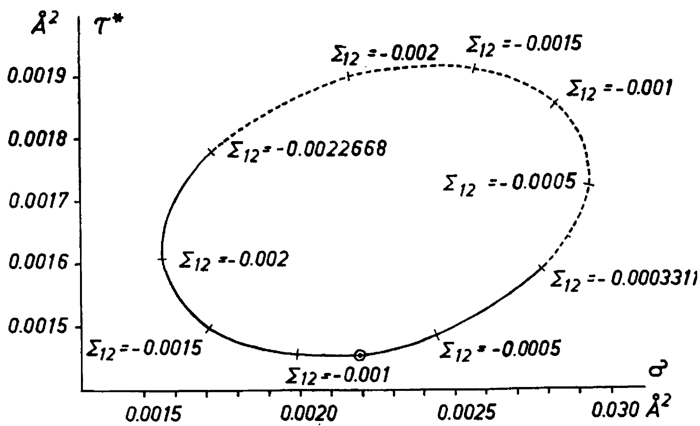


Fig. 4. Values of mean-square amplitudes of vibration at 298 °K for $^{14}NO_2$, consistent with $\omega_1 = 1357.8$ and $\omega_2 = 756.8$ cm^{-1}. ⊙ indicates the best calculated values (see the text).

Table 3. Calculated mean-square amplitude quantities for nitrogen dioxide molecules.

Symbol	Mean-square amplitudes in Å² units for $^{14}NO_2$ $T = 0$	298 °K
Σ_1	0.0010522	0.0010561
Σ_2	0.0072833	0.0076139
Σ_{12}	−0.0007502	−0.0007355
Σ_3	0.0018600	0.0018612
σ	0.0014561	0.0014586
σ'	−0.0004039	−0.0004025
τ	0.0072833	0.0076139
ϱ	−0.0005305	−0.0005201
τ^*	0.0021060	0.0021984
ϱ^*	0.0007632	0.0007709

Symbol	Mean-square amplitudes in Å² units for $^{15}NO_2$ $T = 0$	298 °K
Σ_1	0.0010438	0.0010477
Σ_2	0.0071348	0.0074809
Σ_{12}	−0.0007160	−0.0007026
Σ_3	0.0018187	0.0018201
σ	0.0014312	0.0014339
σ'	−0.0003875	−0.0003862
τ	0.0071348	0.0074809
ϱ	−0.0005063	−0.0004968
τ^*	0.0021249	0.0021975
ϱ^*	0.0007649	0.0007722

These quantities are observable from electron-diffraction (see Ref.[19] and references cited therein), the measurements for nitrogen dioxide being in progress [20]. In the present calculations the quantities in question are obtainable by means of eqns (3) and (12). Fig. 4 shows a graphical representation of all the possible real values of of σ and τ^*.

The best calculated values of mean-square amplitudes were obtained by including the normal frequencies for $^{15}NO_2$. The ten mean-square amplitude quantities defined in this paper were calculated for both $^{14}NO_2$ and $^{15}NO_2$ at the temperatures $T = 0$ and 298 °K. The numerical results are given in Table 3, and some of them indicated on Figs. 3 and 4.

Isotope rules. The normal frequencies given in Table 1 are adjusted to fit accurately the product rule. In consequence, also the isotope rules for mean-square amplitude quantities [11,12] will be fulfilled. In accordance with the theory of the cited papers, one has in the present case

$$\frac{\nu_1\nu_2}{\nu_1{}^*\nu_2{}^*} = \frac{\Sigma_1\Sigma_2-\Sigma_{12}{}^2}{\Sigma_1{}^*\Sigma_2{}^*-(\Sigma_{12}{}^*)^2} = \sqrt{\frac{(2\mu_X + \mu_Y)\mu_Y}{(2\mu_X{}^* + \mu_Y{}^*)\mu_Y{}^*}} \tag{13}$$

$$\frac{\nu_3}{\nu_3{}^*} = \frac{\Sigma_3}{\Sigma_3{}^*} = \sqrt{\frac{2\mu_X\sin^2 A + \mu_Y}{2\mu_X{}^*\sin^2 A + \mu_Y{}^*}} \tag{14}$$

Table 4. Mean amplitudes of vibration in nitrogen dioxide molecules.

Molecule	Distance	Mean amplitude of vibration (Å) $T = 0$	298 °K
$^{14}NO_2$	N–O	0.0382	0.0382
	O...O	0.0459	0.0469
$^{15}NO_2$	N–O	0.0378	0.0379
	O...O	0.0461	0.0469

Here the mean-square amplitude matrix elements are referred to the absolute zero. By inserting the appropriate atomic masses according to $\mu_X = 1/14.00754$, $\mu_X^* = 1/15.00489$ and $\mu_Y = \mu_Y^* = 1/16.00000$, and with the value $2A = 134°15'$, the numerical results 1.0239 and 1.0227 are obtained for the respective ratios of eqns (13) and (14). If the interaction mean-square amplitudes are neglected as an approximation, eqn (13) reduces to

$$\nu_1\nu_2/\nu_1^*\nu_2^* \approx \Sigma_1\Sigma_2/\Sigma_1^*\Sigma_2^* = 1.0290 \tag{15}$$

Mean amplitudes of vibration. In the present notation, the square-roots of σ and τ^* represent the mean amplitudes of vibration for the two types of interatomic distances, such quantities being suitable as parameters in molecular structure studies [19]. In Table 4 the mean amplitudes of vibration from the present calculations for the nitrogen dioxide molecules are given.

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