

Vibrational Mean-Square Amplitude Matrices

XIV. Treatment of Linear Symmetrical X_2Y_2 Molecules with Application to Cyanogen

S. J. CYVIN and E. MEISINGSETH

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

A theoretical treatment of the vibrational mean-square amplitude quantities for linear symmetrical X_2Y_2 molecules is presented. The evaluation of the generalized (parallel and perpendicular) mean-square amplitudes for the four types of interatomic distances is included. Numerical computations for cyanogen are reported, *viz.* those of the mean amplitudes of vibration, and the mean-square parallel and perpendicular amplitudes, the latter ones having been used for calculating the "shrinkage" effects.

The mean-square amplitude matrices¹ have proved to be very useful in spectroscopic calculations, especially those associated with electron-diffraction investigations. In the present paper some studies on cyanogen are reported, which have been actuated by recent electron-diffraction work on this molecule, to be communicated later. The theoretical treatment here presented may also be adapted to butatriene², if this molecule is considered as a linear four-particle structure ($CH_2=C=C=CH_2$).

THEORETICAL TREATMENT

The treatment is based on the assumption of small harmonic vibrations.³ *Symmetry coordinates.* The chosen symmetry coordinates are specified below.

| | |
|---------------------------------|--|
| Symmetry species Σ_g^+ : | $S_1 = 2^{-\frac{1}{2}}(r_1 + r_2)$ |
| | $S_2 = d$ |
| » » Σ_u^+ : | $S_3 = 2^{-\frac{1}{2}}(r_1 - r_2)$ |
| » » Π_g : | $S_{4a} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1 - \alpha_2)$ |
| » » Π_g : | $S_{4b} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1' - \alpha_2')$ |
| » » Π_u : | $S_{5a} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1 + \alpha_2)$ |
| » » Π_u : | $S_{5b} = 2^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(\alpha_1' + \alpha_2')$ |

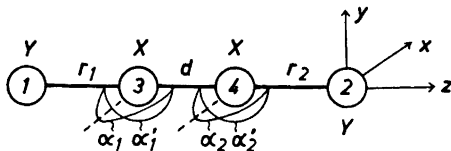


Fig. 1. Notation and orientation used for the linear symmetrical X_2Y_2 molecular model. Notice the numbering of atoms.

Here r_1 and r_2 designate the X—Y stretching coordinates, d designating the X—X stretchings. α_1 and α_2 designate the XXY angle bendings in the xz plane, α_1' and α_2' designating those in the yz plane (see Fig. 1). R and D are used to identify the X—Y and X—X equilibrium distances, respectively.

Cartesian displacement coordinates. With the chosen orientation of the Cartesian coordinate axes and numbering of the atoms (see Fig. 1) the following expressions have been found for the Cartesian displacement coordinates in terms of the symmetry coordinates.

$$\begin{aligned}
 x_1 &= 2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}m_X K^{-1}S_{4a} + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_{5a} \\
 y_1 &= 2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}m_X K^{-1}S_{4b} + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_{5b} \\
 z_1 &= -2^{-\frac{1}{2}}S_1 - \frac{1}{2}S_2 - 2^{-\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_3 \\
 x_2 &= -2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}m_X K^{-1}S_{4a} + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_{5a} \\
 y_2 &= -2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}m_X K^{-1}S_{4b} + 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_{5b} \\
 z_2 &= 2^{-\frac{1}{2}}S_1 + \frac{1}{2}S_2 - 2^{-\frac{1}{2}}m_X(m_X + m_Y)^{-1}S_3 \\
 x_3 &= -2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}[1 + 2(R/D)]m_Y K^{-1}S_{4a} - 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_{5a} \\
 y_3 &= -2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}[1 + 2(R/D)]m_Y K^{-1}S_{4b} - 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_{5b} \\
 z_3 &= -\frac{1}{2}S_2 + 2^{-\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_3 \\
 x_4 &= 2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}[1 + 2(R/D)]m_Y K^{-1}S_{4a} - 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_{5a} \\
 y_4 &= 2^{-\frac{1}{2}}(D/R)^{\frac{1}{2}}[1 + 2(R/D)]m_Y K^{-1}S_{4b} - 2^{-\frac{1}{2}}(R/D)^{\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_{5b} \\
 z_4 &= \frac{1}{2}S_2 + 2^{-\frac{1}{2}}m_Y(m_X + m_Y)^{-1}S_3
 \end{aligned}$$

Here it has been made use of the abbreviation

$$K = (D/R)(m_X + m_Y) + 4[1 + (R/D)]m_Y$$

m_X and m_Y denote the X and Y atomic masses, respectively.

F and G matrices. The set of equations connecting force constants and normal frequencies are given in the book of Herzberg⁴ and shall not be repeated here. The Wilson *G* matrix elements may be evaluated by the standard methods^{3,5-7}. For some aspects of the *GF* matrix treatment of the linear symmetrical X_2Y_2 molecular model in particular, see⁸. For the linear vibrations, see also Ref.⁹

Σ matrix. The six non-vanishing elements of the symmetrized mean-square amplitude matrix ($\Sigma = \langle \tilde{S} \tilde{S} \rangle$) are defined by

$$\begin{aligned}
 \Sigma_1 &= \langle S_1^2 \rangle, \Sigma_2 = \langle S_2^2 \rangle, \Sigma_{12} = \langle S_1 S_2 \rangle, \\
 \Sigma_3 &= \langle S_3^2 \rangle, \Sigma_4 = \langle S_{4a}^2 \rangle = \langle S_{4b}^2 \rangle, \Sigma_5 = \langle S_{5a}^2 \rangle = \langle S_{5b}^2 \rangle
 \end{aligned}$$

One has the following relations for the normal frequencies in terms of the Σ matrix elements.

$$\begin{aligned} \Delta_1 + \Delta_2 &= m_Y \Sigma_1 + \frac{1}{2} (m_X + m_Y) \Sigma_2 + 2^{\frac{1}{2}} m_Y \Sigma_{12} \\ \Delta_1 \Delta_2 &= \frac{1}{2} m_X m_Y (\Sigma_1 \Sigma_2 - \Sigma_{12}^2) \\ \Delta_3 &= m_X m_Y (m_X + m_Y)^{-1} \Sigma_3 \\ \Delta_4 &= m_X m_Y K^{-1} \Sigma_4 \\ \Delta_5 &= (R/D) m_X m_Y (m_X + m_Y)^{-1} \Sigma_5 \end{aligned}$$

The normal frequencies are implied according to

$$\Delta_k = (h/8\pi^2 \nu_k) \coth(h\nu_k/2kT)$$

where h is Planck's constant, k Boltzmann's constant, and T the absolute temperature.

Additional mean-square amplitude quantities. Further mean-square amplitude quantities will be introduced for the parallel vibrations of the considered molecular model, viz.:

$$\begin{aligned} \sigma_r &= \langle r_1^2 \rangle = \langle r_2^2 \rangle, \quad \sigma_{rr} = \langle r_1 r_2 \rangle, \\ \sigma_d &= \langle d^2 \rangle, \quad \sigma_{rd} = \langle r_1 d \rangle = \langle r_2 d \rangle \end{aligned}$$

For these quantities in terms of the Σ matrix elements introduced above, one finds

$$\begin{aligned} \sigma_r &= \frac{1}{2} (\Sigma_1 + \Sigma_3), \quad \sigma_{rr} = \frac{1}{2} (\Sigma_1 - \Sigma_3), \\ \sigma_d &= \Sigma_2, \quad \sigma_{rd} = 2^{\frac{1}{2}} \Sigma_{12} \end{aligned}$$

The quantities σ_r and σ_d represent the mean-square amplitudes of vibration for the (bonded) X—Y and X—X distances, respectively, σ_{rr} and σ_{rd} being the interaction mean-square amplitudes.

For the mean-square amplitudes of vibration for the (non-bonded) X...Y and Y...Y distances one finds

$$\sigma_{r+d} = \sigma_r + \sigma_d + 2\sigma_{rd} = \frac{1}{2} \Sigma_1 + \Sigma_2 + 2^{\frac{1}{2}} \Sigma_{12} + \frac{1}{2} \Sigma_3$$

and

$$\sigma_{r+d} = 2\sigma_r + 2\sigma_{rr} + \sigma_d + 4\sigma_{rd} = 2\Sigma_1 + \Sigma_2 + 8^{\frac{1}{2}} \Sigma_{12}$$

respectively.

Mean-square perpendicular amplitudes and the "shrinkage" effect. The shrinkage effect in linear molecules, which has been observed from electron-diffraction by Bastiansen *et al.*^{2,10,11} may be calculated spectroscopically by means of the mean-square perpendicular amplitudes¹², as has been pointed out by Morino¹³. In the present case of the symmetrical X₂Y₂ molecular model, the following two independent shrinkage effects, given to the first approximation (valid for small harmonic vibrations), will be encountered:

$$\begin{aligned} -\delta_{r+d}^g &= \frac{\tau_{r+d}}{R+D} - \frac{\tau_r}{R} - \frac{\tau_d}{D} \\ -\delta_{2r+d}^g &= \frac{\tau_{2r+d}}{2R+D} - \frac{2\tau_r}{R} - \frac{\tau_d}{D} \end{aligned}$$

Here

$$\tau_r = \langle (x_1 - x_3)^2 \rangle = \langle (x_2 - x_4)^2 \rangle = \langle (y_1 - y_3)^2 \rangle = \langle (y_2 - y_4)^2 \rangle$$

$$\tau_d = \langle (x_3 - x_4)^2 \rangle = \langle (y_3 - y_4)^2 \rangle$$

$$\tau_{r+d} = \langle (x_1 - x_4)^2 \rangle = \langle (x_2 - x_3)^2 \rangle = \langle (y_1 - y_4)^2 \rangle = \langle (y_2 - y_3)^2 \rangle$$

$$\tau_{2r+d} = \langle (x_1 - x_2)^2 \rangle = \langle (y_1 - y_2)^2 \rangle$$

Evaluation of the generalized mean-square amplitudes. Let an arbitrary atom pair ij be considered. The corresponding generalized mean-square amplitudes may be expressed as $\langle (\xi_i - \xi_j)(\eta_i - \eta_j) \rangle$, where $\xi, \eta = x, y$ or z . In the present case the given expressions of the Cartesian displacement coordinates make it possible to detect the transformation coefficients in any expression of the type

$$\xi_i - \xi_j = \sum_n A_{ijn}^{\xi} S_n = \widetilde{A}_{ij}^{\xi} S$$

or

$$\eta_i - \eta_j = \sum_n A_{ijn}^{\eta} S_n = \widetilde{A}_{ij}^{\eta} S$$

Hence the generalized mean-square amplitudes may be evaluated in terms of the Σ matrix elements according to

$$\langle (\xi_i - \xi_j)(\eta_i - \eta_j) \rangle = \widetilde{A}_{ij}^{\xi} \Sigma A_{ij}^{\eta}$$

For the mean-square parallel amplitudes, corresponding to $\xi = \eta = z$, the above given expressions for σ_r , σ_d , σ_{r+d} and σ_{2r+d} are obtained. These expressions, referred to as the mean-square amplitudes of vibration, are identical with the mean-square parallel amplitudes to the first approximation.

As to the mean cross product in the present case, all of them vanish because of symmetry.

The results obtained for the mean-square perpendicular amplitudes are given in the following.

Table 1. Mean-square parallel (σ) and perpendicular (τ) amplitudes for $^{12}\text{C}_2^{14}\text{N}_2$ at $T = 0$ and 298°K .

| Distance | Symbol | Generalized mean-square amplitudes (\AA^2 units) | |
|--------------|-----------------|---|---------------------|
| | | $T = 0$ | 298°K |
| C \equiv N | σ_r | 0.001215 | 0.001217 |
| | τ_r | 0.007590 | 0.012955 |
| C—C | σ_d | 0.001730 | 0.001758 |
| | τ_d | 0.004948 | 0.005885 |
| C \cdots N | σ_{r+d} | 0.002055 | 0.002102 |
| | τ_{r+d} | 0.006006 | 0.011082 |
| N \cdots N | σ_{2r+d} | 0.002381 | 0.002452 |
| | τ_{2r+d} | 0.000507 | 0.000603 |

Table 2. Mean amplitudes of vibration for $^{12}\text{C}_2^{14}\text{N}_2$ at $T = 0$ and 298°K .

| Distance | Symbol | Mean amplitude of vibration (Å units) | |
|--------------------------|------------|--|---------------------|
| | | $T = 0$ | 298°K |
| $\text{C}\equiv\text{N}$ | u_r | 0.0349 | 0.0349 |
| $\text{C}-\text{C}$ | u_d | 0.0416 | 0.0419 |
| $\text{C}\cdots\text{N}$ | u_{r+d} | 0.0453 | 0.0458 |
| $\text{N}\cdots\text{N}$ | u_{2r+d} | 0.0488 | 0.0495 |

$$\tau_r = \frac{1}{2}(D/R)\{m_x + [1 + (R/D)]m_y\}^2 K^{-2} \Sigma_4 + \frac{1}{2}(R/D)\Sigma_5$$

$$\tau_d = 2(D/R)[1 + 2(R/D)]^2 m_y^2 K^{-2} \Sigma_4$$

$$\tau_{r+d} = \frac{1}{2}(D/R)\{m_x - [1 + 2(R/D)]m_y\}^2 K^{-2} \Sigma_4 + \frac{1}{2}(R/D)\Sigma_5$$

$$\tau_{2r+d} = 2(D/R)m_x^2 K^{-2} \Sigma_4$$

For the meaning of K , see the above section of Cartesian displacement coordinates.

NUMERICAL COMPUTATIONS FOR CYANOGEN

The adopted values for the equilibrium interatomic distances are $R = 1.157$ Å for $\text{C}\equiv\text{N}$ ^{14,15} and $D = 1.380$ Å for $\text{C}-\text{C}$ ¹⁵, which are not much different from the values used by Langseth and Møller¹⁶ in their calculations of the potential constants for cyanogen. In the present calculations the interaction force constant value $F_{12} = 0.08485$ mdyne/Å (referred to the symmetry coordinate system) was taken from Langseth and Møller¹⁶. To determine the remaining force constants, the $^{12}\text{C}_2^{14}\text{N}_2$ vibrational frequencies taken from the same paper¹⁶ were applied, *viz.* Raman frequencies from the investigation of the mentioned authors¹⁶, together with some earlier infrared frequencies¹⁷. The final values showed only slight deviations from those of Langseth and Møller¹⁶, mainly due to the different equilibrium parameters employed.*

Table 3. Shrinkage effect for $^{12}\text{C}_2^{14}\text{N}_2$ at $T = 0$ and 298°K .

| Distance | Symbol | Shrinkage effect (Å units) | |
|--------------------------|-------------------|----------------------------|---------------------|
| | | $T = 0$ | 298°K |
| $\text{C}\cdots\text{N}$ | δ_{r+d}^g | 0.008 | 0.011 |
| $\text{N}\cdots\text{N}$ | δ_{2r+d}^g | 0.017 | 0.024 |

* The present values are $F_1 = 15.654$, $F_2 = 7.308$, $F_{12} = 0.08485$ and $F_3 = 17.582$ for the linear vibrational force constants, all in mdyne/Å. It should be noticed that Langseth and Møller¹⁶ uses different symmetry coordinates from the present ones. In terms of their notation for the potential constants, one has: $F_1 = 4a_{11}$, $F_2 = 2(a_{11} + a_{22} + 2a_{12})$, $F_{12} = 8\frac{1}{2}(a_{11} + a_{12})$, and $F_3 = 4a_{33}$.

The Σ matrix elements were calculated according to ¹

$$\Sigma = L \Delta \widetilde{L}$$

where L is the normal coordinate transformation matrix ($S = LQ$) and has been determined by the standard method of characteristic vectors ³. The final results, obtained by means of the Σ matrix elements, are presented in Tables 1–3. Table 1 shows the mean-square parallel and perpendicular amplitudes for the four types of interatomic distances. Table 2 shows the mean amplitudes of vibration for the same types of distances, viz. $u_{X-Y} = \sigma_r^{\frac{1}{2}}$, $u_{X-X} = \sigma_d^{\frac{1}{2}}$, $u_{X\dots Y} = \sigma_{r+d}^{\frac{1}{2}}$ and $u_{Y\dots Y} = \sigma_{2r+d}^{\frac{1}{2}}$. Finally, in Table 3 the calculated shrinkage effects are shown.

It is intended to compare the presently calculated mean amplitudes of vibration and shrinkage effects with the results from an electron-diffraction investigation now in progress.

REFERENCES

1. Previous articles of this series: Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 828, 835, 958; *Acta Chem. Scand.* **13** (1959) 1397, 1400, 1809; *J. Mol. Spectroscopy* **5** (1960) 38.
2. Almenningen, A., Bastiansen, O. and Trættemberg, M. *Acta Chem. Scand.* *In press.*
3. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw-Hill Book Co., New York 1955.
4. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, D. van Nostrand Co. New York 1945.
5. Wilson, E. B., Jr. *J. Chem. Phys.* **9** (1941) 76.
6. Decius, J. C. *J. Chem. Phys.* **11** (1948) 1025.
7. Ferigle, S. M. and Meister, A. G. *J. Chem. Phys.* **19** (1951) 982.
8. Cleveland, F. F. and Meister, A. G. *J. chim. phys.* **46** (1949) 108.
9. Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 341.
10. Almenningen, A., Bastiansen, O. and Munthe-Kaas, T. *Acta Chem. Scand.* **10** (1956) 261.
11. Almenningen, A., Bastiansen, O. and Trættemberg, M. *Acta Chem. Scand.* **13** (1959) 1699.
12. Morino, Y. and Hirota, E. *J. Chem. Phys.* **23** (1955) 737.
13. Morino, Y. *Private communications.*
14. Westenberg, A. A. and Wilson, E. B., Jr. *J. Am. Chem. Soc.* **72** (1950) 109.
15. Møller, C. K. and Stoicheff, B. P. *Can. J. Phys.* **32** (1954) 635.
16. Langseth, A. and Møller, C. K. *Acta Chem. Scand.* **4** (1950) 725.
17. Bailey, C. R. and Carsons, S. C. *J. Chem. Phys.* **7** (1939) 859.

Received February 7, 1961.