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Mean Amplitudes of Vibration and Shrinkage Effect of Hydrogen Cyanide from Spectroscopic Data

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Some aspects of the molecular vibrations of the linear YXZ molecular model are studied, and the following calculated quantities for hydrogen cyanide are reported: (*a*) Force constants, (*b*) L matrix elements, (*c*) various mean-square amplitude quantities, (*d*) mean amplitudes of vibration, and (*e*) Bastiansen-Morino shrinkage effect. It has been found at 298°K in Å units: (*d*) $u_{CH} = 0.0731$, $u_{CN} = 0.0342$, $u_{HN} = 0.0941$, and (*e*) $\delta = 0.0164$.

Some spectroscopic calculations for hydrogen cyanide have been performed in addition to the study of cyanogen [1] and acetylene [2]. These computations are believed to be of great value in connection with the recent electron-diffraction study of cyanoacetylene.

THEORY

The present computations are based on the assumption of small harmonic vibrations [3]. It is adhered to the previously chosen internal coordinates as communicated by Cyvin [4].

The cartesian displacement coordinates have been expressed in terms of the symmetry coordinates with the following result.

$$
\begin{aligned}
x_X &= -S_{2a}(R_1R_2)^{1/2}(R_1 + R_2)m_Y m_Z/C \\
y_X &= -S_{2b}(R_1R_2)^{1/2}(R_1 + R_2)m_Y m_Z/C \\
z_X &= (S_1 m_Y - S_3 m_Z)/(m_X + m_Y + m_Z) \\
x_Y &= S_{2a}(R_1R_2)^{1/2}R_2 m_X m_Z/C \\
y_Y &= S_{2b}(R_1R_2)^{1/2}R_2 m_X m_Z/C \\
z_Y &= -[S_1(m_X + m_Z) + S_3 m_Z]/(m_X + m_Y + m_Z) \\
x_Z &= S_{2a}(R_1R_2)^{1/2}R_1 m_X m_Y/C \\
y_Z &= S_{2b}(R_1R_2)^{1/2}R_1 m_X m_Y/C \\
z_Z &= [S_1 m_Y + S_3(m_X + m_Y)]/(m_X + m_Y + m_Z)
\end{aligned}
$$

Here m_X, m_Y and m_Z denote the atomic masses of the X, Y and Z atoms, respectively. The following abbreviation has been used:

$$C = R_1^2\, m_X m_Y + R_2^2\, m_X m_Z + (R_1 + R_2)^2\, m_Y m_Z$$

R_1 and R_2 are used to designate the equilibrium X—Y and X—Z distances, respectively. For further explanation of the symbols, the cited paper [4] should be consulted.

Parallel vibrations. The mean-square parallel amplitudes (or mean-square amplitudes of vibration [5]) for the presently treated molecular model have been studied previously [6]. With the notation $\sigma_{AB} = \langle(z_A - z_B)^2\rangle$, where X, Y and Z may be inserted for A and B, one has

$$\sigma_{XY} = \Sigma_1, \quad \sigma_{XZ} = \Sigma_3, \quad \sigma_{YZ} = \Sigma_1 + \Sigma_3 + 2\,\Sigma_{13}$$

Perpendicular vibrations. The mean-square perpendicular amplitudes [1,4,7] will be identified by the symbol $\tau_{AB} = \langle(x_A - x_B)^2\rangle = \langle(y_A - y_B)^2\rangle$. The following expressions have been found in terms of the mean-square amplitude matrix element $\Sigma_2 = \langle S_{2a}^2\rangle = \langle S_{2b}^2\rangle$.

$$\tau_{XY} = \Sigma_2 R_1 R_2 m_Z^2 [R_2 m_X + (R_1 + R_2) m_Y]^2 / C^2$$
$$\tau_{XZ} = \Sigma_2 R_1 R_2 m_Y^2 [R_1 m_X + (R_1 + R_2) m_Z]^2 / C^2$$
$$\tau_{YZ} = \Sigma_2 R_1 R_2 m_X^2 (R_1 m_Y - R_2 m_Z)^2 / C^2$$

The Σ_2 element is closely connected with the perpendicular vibration frequency (ω_2) according to

$$\Sigma_2 = (hC/8\pi^2 R_1 R_2 m_X m_Y m_Z c\omega_2)\, \coth(hc\omega_2/2kT)$$

where, apart from the symbols used above, only the temperature (T in °K) and fundamental physical constants (h = Planck's constant, c = velocity of light, k = Boltzmann's constant) are present.

Shrinkage effect [1,2,8]. In the presently considered molecular model the Bastiansen-Morino shrinkage effect is given by

$$-\delta = \tau_{YZ}/(R_1 + R_2) - \tau_{XY}/R_1 - \tau_{XZ}/R_2$$

NUMERICAL COMPUTATIONS

The theory has been applied to hydrogen cyanide, identifying the atoms X, Y and Z by C, H and N, respectively.

The adopted equilibrium distance values, *viz.*, $R_1 = 1.0630$ Å and $R_2 = 1.1538$ Å, have been taken from Costain [9]. The normal frequencies (see below) have been obtained from the reported data of Allen, Tidwell and Plyler [10], and are not much different from those of Douglas and Sharma [11].

No.	HCN	DCN
1	2127.6 cm^{-1}	1953.2 cm^{-1}
2	726.8 cm^{-1}	579.9 cm^{-1}
3	3442.8 cm^{-1}	2702.9 cm^{-1}

The force constants were recalculated with the following result (in the notation of Ref.[10]):

$f_1 = 6.249 \times 10^5$ d/cm, $\quad f_2 = 18.689 \times 10^5$ d/cm,
$f_{12} = -0.2140 \times 10^5$ d/cm, $\quad f_a/R_1R_2 = 0.2108 \times 10^5$ d/cm.

The wide applicability of the L-matrix makes it justified to specify its ele-

Table 1. Mean-square amplitude quantities in Å² units for hydrogen cyanide.

Symbol	$T = 0$	298°K
$\Sigma_1 = \sigma_{CH}$	0.005345	0.005345
$\Sigma_3 = \sigma_{CN}$	0.001167	0.001167
Σ_{13}	0.001169	0.001170
Σ_2	0.03425	0.03637
σ_{HN}	0.008852	0.008852
τ_{CH}	0.02264	0.02403
τ_{CN}	0.000870	0.000924
τ_{HN}	0.01463	0.01554

Table 2. Mean amplitudes of vibration (u) and shrinkage effect (δ) in Å units for hydrogen cyanide.

Symbol	$T = 0$	298°K
u_{CH}	0.0731	0.0731
u_{CN}	0.0342	0.0342
u_{HN}	0.0941	0.0941
δ	0.0154	0.0164

ments for the symmetry coordinates of the species Σ^+. It has been found in $(\text{Amu})^{-\frac{1}{2}}$:

$$S_1 = 0.1614\ Q_1 + 1.024\ Q_3$$
$$S_3 = 0.3678\ Q_1 + 0.1393\ Q_3$$

The elements of the Σ-matrix are given numerically in Table 1 at the temperatures of absolute zero and 298°K, along with the mean-square parallel and perpendicular amplitudes. In Table 2 the mean amplitudes of vibration and the shrinkage effect are given.

REFERENCES

1. Cyvin, S. J. and Meisingseth, E. *Acta Chem. Scand.* **15** (1961) 1289.
2. Meisingseth, E. and Cyvin, S. J. *Acta Chem. Scand.* **15** (1961) 2021.
3. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw-Hill Book, New York 1955.
4. Cyvin, S. J. *Spectrochim. Acta* **17** (1961) 1219.
5. Cyvin, S. J. *Kgl. Norke Videnskab. Selskabs Skrifter* (1959) No. 2.
6. Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 835.
7. Morino, Y. and Hirota, E. *J. Chem. Phys.* **23** (1955) 737; Cyvin, S. J. *J. Mol. Spectroscopy* **6** (1961) 333.
8. Bastiansen, O. and Trætteberg, M. *Acta Cryst.* **13** (1960) 1108; Morino, Y. *Acta Cryst.* **13** (1960) 1107.
9. Costain, C. C. *J. Chem. Phys.* **29** (1958) 864.
10. Allen, H. C., Jr., Tidwell, E. D. and Plyler, E. K. *J. Chem. Phys.* **25** (1956) 302.
11. Douglas, A. E. and Sharma, D. *J. Chem. Phys.* **21** (1953) 448.

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