

MEAN AMPLITUDES OF VIBRATION: PYRAMIDAL XYZ₂ MOLECULES

BY DR. K. VENKATESWARLU, F.A.Sc.

AND

DR. K. V. RAJALAKSHMI

(Department of Physics, Kerala University, C/o U.C. College, Alwaye, S. India)

Received August 22, 1964

ABSTRACT

The theory of mean square amplitude of vibration using the symmetry co-ordinates has been applied to the pyramidal XYZ₂ molecular model. The elements of the mean square amplitude matrices and the mean amplitude quantities at 300° K. for thionyl halides have been reported.

1. INTRODUCTION

THE normal vibrations of thionyl halides belonging to the pyramidal XYZ₂ type have been studied by a few authors¹⁻⁴ using different types of potential force fields. In the present study, the mean square amplitude matrices have been derived for the pyramidal XYZ₂ molecular model on the assumption of a harmonic force field and the mean amplitudes of vibration for SOF₂, SOCl₂ and SOBr₂ have been evaluated at 300° K. from their vibrational frequencies.

2. MOLECULAR SYMMETRY

The pyramidal XYZ₂ molecules belong to C_s symmetry and thus have 4a' + 2a'' types of vibration.

The symmetry co-ordinates and the elements of the G matrix used here are those given by Venkateswarlu and Rajalakshmi.⁴ But in calculating the mean amplitudes, proper account of the equilibrium bond length has been taken.

3. SYMMETRIZED MEAN SQUARE AMPLITUDE MATRIX

The symmetrized mean square amplitude matrix Σ involves the following mean square amplitude quantities.

$$\begin{array}{ll}
 \Sigma_{11} = \sigma_R & \Sigma_{12} = \sigma_{R\beta} \\
 \Sigma_{22} = \sigma_\beta & \Sigma_{13} = \sqrt{2} \sigma_{Rr} \\
 \Sigma_{33} = \sigma_r + \sigma_{rr} & \Sigma_{14} = \sqrt{2} \sigma_{Ra} \\
 \Sigma_{44} = \sigma_a + \sigma_{aa} & \Sigma_{23} = \sqrt{2} \sigma_{r\beta} \\
 \Sigma_{55} = \sigma_r - \sigma_{rr} & \Sigma_{24} = \sqrt{2} \sigma_{a\beta} \\
 \Sigma_{66} = \sigma_a - \sigma_{aa} & \Sigma_{34} = \sigma_{ra} + \sigma'_{ra} \\
 & \Sigma_{56} = \sigma_{ra} - \sigma'_{ra}
 \end{array}$$

where the entering quantities are defined by the mean values of the square of the changes in bond lengths and bond angles.

4. ADDITIONAL MEAN SQUARE AMPLITUDES

Considering the nonbonded distance deviations ΔR^* and Δr^* between Y...Z and Z...Z atoms respectively, the additional mean square amplitudes σ_{R^*} , σ_{r^*} , $\sigma_{R^*r^*}$, σ_{RR^*} , σ_{Rr^*} , σ_{rR^*} and σ_{rr^*} are obtained. These additional mean square amplitude quantities can be expressed in terms of the symmetrized mean square amplitude matrix elements. The relations obtained for σ_{r^*} and σ_{R^*} are given in the following:

$$\begin{aligned}
 \sigma_{r^*} &= 2 \Sigma_{33} \sin^2(\beta/2) + \Sigma_{22} \cos^2(\beta/2) + \sqrt{2} \Sigma_{23} \sin \beta \\
 \sigma_{R^*} &= (R^*)^{-2} \left[\frac{1}{2} (\Sigma_{33} + \Sigma_{55}) (r - R \cos \alpha)^2 \right. \\
 &\quad + \Sigma_{11} (R - r \cos \alpha)^2 \\
 &\quad + \frac{1}{2} Rr (\Sigma_{44} + \Sigma_{66}) \sin^2 \alpha \\
 &\quad + \sqrt{2} \Sigma_{13} (r - R \cos \alpha) (R - r \cos \alpha) \\
 &\quad + (Rr)^{\frac{1}{2}} (\Sigma_{34} + \Sigma_{56}) (r - R \cos \alpha) \sin \alpha \\
 &\quad \left. + \sqrt{2} \Sigma_{14} (R - r \cos \alpha) \sin \alpha \right]
 \end{aligned}$$

where

$$R^* = (R^2 + r^2 - 2Rr \cos \alpha)^{\frac{1}{2}}$$

Similar expressions can be derived for the other additional mean square amplitude quantities also.

5. RESULTS

The molecular parameters⁶ and observed frequencies for SOF_2 , SOCl_2 and SOBr_2 are listed in Table I.

TABLE I

Molecular parameters and observed frequencies (cm.⁻¹) for
SOF₂, SOCl₂ and SOBr₂

| Molecule | Molecular parameters | | | | Observed frequencies (cm. ⁻¹) | | | | | |
|-------------------------------------|----------------------|-------|----------|---------|---|------------------------------|----------------|----------------|-------------------------------|----------------|
| | R Å | r Å | α | β | σ ₁ | σ ₂ ^{a'} | σ ₃ | σ ₄ | σ ₅ ^{a''} | σ ₆ |
| SOF ₂ ^{6,7} | 1.412 | 1.585 | 109° 49' | 92° 49' | 1308 | 801 | 526 | 326 | 721 | 393 |
| SOCl ₂ ^{6,8-10} | 1.450 | 2.070 | 106° | 114° | 1229 | 490 | 194 | 344 | 443 | 284 |
| SOBr ₂ ¹¹ | 1.450 | 2.27 | 108° | 96° | 1121 | 405 | 120 | 267 | 379 | 223 |

The mean square amplitude quantities are evaluated using the secular equation¹²

$$|\Sigma G^{-1} - \Delta E| = 0$$

where G⁻¹ is the inverse of the kinetic energy matrix G and

$$\Delta k = \frac{h}{8\pi^2 \nu_k} \coth \left(\frac{h\nu_k}{2kT} \right).$$

Here *h* is Planck's constant, *k* Boltzmann's constant and *T* the temperature in degree Kelvin.

The mean square amplitude quantities for SOF₂, SOCl₂ and SOBr₂ are listed in Table II.

The mean amplitudes for the bonded and nonbonded distance deviations are given in Table III.

In the force constant calculations⁴ of thionyl halides, it was found that S = 0 stretching force constant shows a marked diminution in the value from SOF₂ to SOBr₂, probably due to the increasing electronegativity of the halogen group from F to Br on sulphur atom. But the S = 0 mean amplitude of vibration in these molecules shows only a small increase from SOF₂ to SOBr₂. It is found that the sulphur-halogen mean amplitude of vibration increases from lower to higher member of the halogen group. The same trend is noticed in the case of the nonbonded mean amplitude quantities also.

TABLE II

Mean square amplitude quantities in Å² for SOF₂, SOCl₂ and SOBr₂ at 300°K.

| Symbol | Mean square amplitude (Å ²) | | |
|--------------------|---|-------------------|-------------------|
| | SOF ₂ | SOCl ₂ | SOBr ₂ |
| σ_R | 0.001556 | 0.001565 | 0.001578 |
| σ_F | 0.001895 | 0.002906 | 0.003178 |
| σ_β | 0.005658 | 0.006034 | 0.012090 |
| σ_a | 0.012025 | 0.023105 | 0.018320 |
| σ_{RF} | -0.000043 | -0.000072 | -0.000059 |
| σ_{FF} | -0.000233 | -0.000415 | -0.000603 |
| $\sigma_{R\beta}$ | 0.000066 | 0.000133 | 0.000101 |
| σ_{Ra} | -0.000058 | -0.000069 | -0.000147 |
| $\sigma_{r\beta}$ | 0.000537 | 0.000287 | 0.001036 |
| σ_{ra} | -0.000549 | -0.003033 | -0.001176 |
| σ'_{ra} | 0.000013 | 0.000214 | 0.000157 |
| $\sigma_{a\beta}$ | 0.000008 | 0.000010 | 0.000011 |
| σ_{aa} | 0.000145 | 0.000045 | 0.000090 |
| σ_z^* | 0.005860 | 0.007635 | 0.008439 |
| σ_r^* | 0.005959 | 0.006570 | 0.010316 |
| σ_{Rr}^{**} | 0.001061 | 0.000543 | 0.001887 |
| σ_{RR}^* | 0.001139 | 0.001005 | 0.000962 |
| σ_{Rr}^* | -0.000041 | -0.000048 | -0.000051 |
| σ_{rk}^* | 0.001212 | 0.001553 | 0.002460 |
| σ_{rr}^* | 0.001574 | 0.001967 | 0.002607 |

TABLE III

Mean amplitudes in Å for SOF₂, SOCl₂ and SOBr₂ at 300°K.

| Pair | Mean amplitude (Å) | | |
|-------|--------------------|-------------------|-------------------|
| | SOF ₂ | SOCl ₂ | SOBr ₂ |
| X-Y | 0.03945 | 0.03957 | 0.03972 |
| X-Z | 0.04354 | 0.05392 | 0.05637 |
| Y...Z | 0.07654 | 0.08738 | 0.09185 |
| Z...Z | 0.07720 | 0.08106 | 0.10160 |

ACKNOWLEDGMENT

One of the authors (K. V. R.) wishes to thank the Council of Scientific and Industrial Research (Government of India) for the award of a Senior Research Fellowship.

REFERENCES

1. Venkateswarlu, K. and Sundaram, S. *J. Chem. Phys.*, 1957, **54**, 202.
2. —, Thirugnana-sambandam, P. and Balasubramanian, C. *Z. für. Phys. Chem.*, 1961, **218**, 310.
3. Cotton, F. A. and Horrocks, N. D. *Spectrochim. Acta*, 1960, **16**, 358.
4. Venkateswarlu, K. and Rajalakshmi, K. V. *J. Sci. Industr. Res.*, 1962, **21 B**, 349.
5. *Tables of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London, 1958.
6. Gillespie, R. J. and Robinson, E. A. *Can. J. Chem.*, 1961, **39**, 2171.
7. O'Loane, J. K. and Wilson, M. K. *J. Chem. Phys.*, 1955, **23**, 1313.
8. McDowell, C. A. *Trans. Faraday Soc.*, 1953, **49**, 371.
9. Gerding, H., Smit, E. and Westrik, R. *Rec. trav. chim.*, 1941, **60**, 513.
10. Allen, G. and McDowell, C. A. *J. Chem. Phys.*, 1955, **23**, 209.
11. Stammereich, H., Forneris, R. and Tavares, Y. *Ibid.*, 1956, **25**, 1277.
12. Cyvin, S. J. *Acta Polytechnica Scand.*, Ph. **6**, (279/1960).