MEAN AMPLITUDES OF VIBRATION : MOLECULES OF THE LINEAR AND PLANAR AXYZ TYPE

By Dr. K. Venkateswarlu, F.A.Sc.

AND

Miss V. Malathy Devi

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

Received August 22, 1964

Abstract

Applying Cyvin's secular equation method the mean-square amplitude quantities are calculated for molecules of the linear and planar AXYZ type belonging to the symmetry C_s. The mean amplitude values for HN_3, DN_3, HNCS, HNCO, HCOF and DCOF molecules are evaluated at 300° K.

1. Introduction

Mean amplitudes of vibration from spectroscopic data are based on the assumption of small harmonic vibrations. The mean amplitude values will be very useful in defining the non-rigid model of the polyatomic molecules. A precise knowledge of some mean amplitudes of vibration of molecule may serve as additional information to the normal frequencies, for determining the force constants of the molecule.

In the present work, Cyvin's[1] secular equation method has been applied for evaluating the mean amplitudes of linear and planar AXYZ type molecules at 300° K from their vibrational frequencies. The values of mean-square amplitudes and mean amplitudes for the bonded and non-bonded distances for HN_3, DN_3, HNCO and HNCS of the linear AXYZ and for HCOF and DCOF of the planar AXYZ type molecules are reported here for the first time. In calculating the mean amplitude quantities the angle displacements have been multiplied by the appropriate equilibrium bond lengths.

The AXYZ type molecules belong to the symmetry group C_s. The molecular models are represented in Figs. 1 and 2. The normal modes of vibration of this type of molecules are distributed under the two species, 5A′ + 1A″. The latter is an out-of-plane vibration. The symmetry co-ordinates and the elements of the kinetic energy matrices used here for the linear AXYZ molecules are those given by Venkateswarlu and Thirugnanasambandam[2] and those of the planar AXYZ type are the same as reported by Thomas.[3]

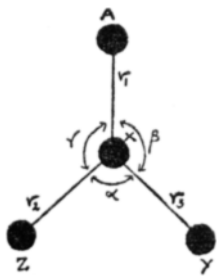

FIG. 1.

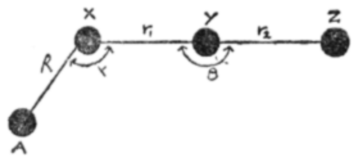

FIG. 2.

FIGS. 1–2. Geometrical configuration of AXYZ type molecule. Fig. 1. Linear AXYZ. Fig. 2. Planar AXYZ.

2. SYMMETRIZED MEAN-SQUARE AMPLITUDE MATRIX

The elements of the symmetrized matrix Σ containing the mean-square amplitude quantities σ of the internal co-ordinates and the nonbonded distances are given as:

Linear AXYZ Type

$$\Sigma_{11} = \sigma_R$$

$$\Sigma_{22} = \tfrac{1}{2}(\sigma_{r_1} + \sigma_{r_2} - 2\sigma_{r_1 r_2})$$

$$\Sigma_{33} = \tfrac{1}{2}(\sigma_{r_1} + \sigma_{r_2} + 2\sigma_{r_1 r_2})$$

$$\Sigma_{44} = \sigma_\alpha$$

$$\Sigma_{55} = \sigma_\theta$$

$$\Sigma_{12} = \frac{1}{\sqrt{2}}(\sigma_{Rr_1} - \sigma_{Rr_2})$$

$$\Sigma_{13} = \frac{1}{\sqrt{2}}(\sigma_{Rr_1} + \sigma_{Rr_2})$$

$$\Sigma_{14} = \sigma_{R\alpha}$$

$$\Sigma_{23} = \tfrac{1}{2}(\sigma_{r_1} - \sigma_{r_2})$$

$$\Sigma_{24} = \frac{1}{\sqrt{2}}(\sigma_{r_1\alpha} - \sigma_{r_2\alpha})$$

$$\Sigma_{34} = \frac{1}{\sqrt{2}}(\sigma_{r_1\alpha} + \sigma_{r_2\alpha}). \quad (1)$$

Planar AXYZ Type

$$\Sigma_{11} = \sigma_{r_1}$$

$$\Sigma_{22} = \sigma_{r_2}$$

$$\Sigma_{33} = \sigma_{r_3}$$

$$\Sigma_{44} = \tfrac{1}{6}\,(4\sigma_{\alpha} - 4\sigma_{\alpha\beta} + \sigma_{\beta} + 2\sigma_{\beta\gamma} + \sigma_{\gamma} - 4\sigma_{\alpha\gamma})$$

$$\Sigma_{55} = \tfrac{1}{2}\,(\sigma_{\beta} + \sigma_{\gamma} - 2\sigma_{\beta\gamma})$$

$$\Sigma_{12} = \sigma_{r_1 r_2}$$

$$\Sigma_{13} = \sigma_{r_1 r_3}$$

$$\Sigma_{23} = \sigma_{r_2 r_3}$$

$$\Sigma_{45} = \frac{1}{\sqrt{12}}\,(2\sigma_{\alpha\beta} - 2\sigma_{\alpha\gamma} - \sigma_{\beta} + \sigma_{\gamma}). \qquad (2)$$

The rest of the elements in equations (1) and (2) are equal to zero. In equations (1) and (2) the entering quantities are defined by the mean values of the changes in bond lengths and bond angles.

3. ADDITIONAL MEAN-SQUARE AMPLITUDES

Considering the interatomic displacements between nonbonded pairs of atoms, the following additional mean-square amplitude quantities are obtained.

Linear AXYZ Type

In the case of linear AXYZ type molecules, $\triangle R^*$ and $\triangle D^*$ denote the nonbonded mean-square amplitude values between A...Y and A...Z atoms respectively and in the case of planar AXYZ molecules $\triangle R^*$, $\triangle D^*$ and $\triangle T^*$ represent the nonbonded mean-square amplitude quantities between A...Z, Y...Z and A...Z atom pairs respectively.

Linear AXYZ Type

$$\sigma_{R^*} = \langle(\triangle R^*)^2\rangle$$

$$\sigma_{D^*} = \langle(\triangle D^*)^2\rangle$$

$$\sigma_{RR^*} = \langle(\triangle R)\,(\triangle R^*)\rangle$$

$$\sigma_{RD^*} = \langle(\triangle R)\,(\triangle D^*)\rangle$$

$$\sigma_{r_1 R^*} = \langle(\triangle r_1)\,(\triangle R^*)\rangle$$

$$\sigma_{r_1 D^*} = \langle(\triangle r_1)(\triangle D^*)\rangle$$

$$\sigma_{r_2 R^*} = \langle(\triangle r_2)(\triangle R^*)\rangle$$

$$\sigma_{r_2 D^*} = \langle(\triangle r_2)(\triangle D^*)\rangle$$

$$\sigma_{R^* D^*} = \langle(\triangle R^*)(\triangle D^*)\rangle.$$

The additional mean-square amplitude quantities are obtained in terms of the symmetrized mean-square amplitude matrix elements. The relations obtained for nonbonded mean-square amplitude quantities σ_{R^*} and σ_{D^*} in terms of the symmetrized mean-square amplitude matrix elements are given as:

$$\sigma_{R^*} = (R^*)^{-2}\Big[(R - r_1 \cos \alpha)^2 \Sigma_{11} + (r_1 - R\cos\alpha)^2 \times \frac{\Sigma_{22} + \Sigma_{33} + 2\Sigma_{23}}{2} + Rr_1 \,.\, \Sigma_{44} \sin^2\alpha$$
$$+ \sqrt{2}(\Sigma_{12} + \Sigma_{13})(R - r_1\cos\alpha)(r_1 - R\cos\alpha)$$
$$+ \sqrt{2}(Rr_1)^{\frac{1}{2}}(\Sigma_{24} + \Sigma_{34})(r_1 - R\cos\alpha)\sin\alpha$$
$$+ 2(Rr_1)^{\frac{1}{2}}(R - r_1\cos\alpha)\Sigma_{14}\sin\alpha\Big]$$

$$\sigma_{D^*} = (D^*)^{-2}\Big[(R - x\cos\alpha)^2\Sigma_{11} + 2\Sigma_{33}(x - R\cos\alpha)^2$$
$$+ \left(\frac{R}{r_1}\right) . x^2 . \Sigma_{44}\sin^2\alpha + 2\sqrt{2}(R - x\cos\alpha)(x - R\cos\alpha)$$
$$+ 2\left(\frac{R}{r_1}\right)^{\frac{1}{2}} x . \Sigma_{14}(R - x\cos\alpha)\sin\alpha$$
$$+ 2\sqrt{2}\,\Sigma_{34}\left(\frac{R}{r_1}\right)^{\frac{1}{2}} x . (x - R\cos\alpha)\sin\alpha\Big]$$

where,

$$R^* = (R^2 + r_1^2 - 2Rr_1\cos\alpha)^{\frac{1}{2}}$$

$$D^* = [R^2 + (r_1 + r_2)^2 - 2R(r_1 + r_2)\cos\alpha]^{\frac{1}{2}}$$

and

$$x = (r_1 + r_2).$$

Similar expressions are derived for the other additional mean-square amplitude quantities also.

Planar AXYZ Type

$$\sigma_{R^*} = \langle(\triangle R^*)^2\rangle$$

$$\sigma_{D^*} = \langle(\triangle D^*)^2\rangle$$

$$\sigma_{T^*} = \langle(\triangle T^*)^2\rangle$$

$$\sigma_{r_1 R^*} = \langle(\triangle r_1)(\triangle R^*)\rangle$$

$$\sigma_{r_1 D^*} = \langle(\triangle r_1)(\triangle D^*)\rangle$$

$$\sigma_{r_1 T^*} = \langle(\triangle r_1)(\triangle T^*)\rangle$$

$$\sigma_{r_2 R^*} = \langle(\triangle r_2)(\triangle R^*)\rangle$$

$$\sigma_{r_2 D^*} = \langle(\triangle r_2)(\triangle D^*)\rangle$$

$$\sigma_{r_2 T^*} = \langle(\triangle r_2)(\triangle T^*)\rangle$$

$$\sigma_{r_3 R^*} = \langle(\triangle r_3)(\triangle R^*)\rangle$$

$$\sigma_{r_3 D^*} = \langle(\triangle r_3)(\triangle D^*)\rangle$$

$$\sigma_{r_3 T^*} = \langle(\triangle r_3)(\triangle T^*)\rangle.$$

The expressions derived for σ_{R^*}, σ_{D^*} and σ_{T^*}, the nonbonded mean-square amplitude quantities between A···Z, Y...Z and A...Y atoms respectively, in terms of the symmetrized mean-square amplitude matrix elements are given below.

$$\sigma_{R^*} = (R^*)^{-2}\Big[(r_1 - r_2\cos\gamma)^2\Sigma_{11} + (r_2 - r_1\cos\gamma)^2\Sigma_{22}$$

$$+ \left\{\left(\frac{r_2}{r_3}\right)\frac{\Sigma_{55}}{2} + \frac{\Sigma_{44}}{6}\cdot\frac{1}{r_3^2} + 2\left(\frac{r_2}{r_3}\right)^{\frac{1}{2}}\cdot\frac{1}{r_3}\frac{\Sigma_{45}}{\sqrt{12}}\right\}\sin^2\gamma$$

$$+ 2(r_1 - r_2\cos\gamma)(r_2 - r_1\cos\gamma)\Sigma_{12}$$

$$- 2(r_1 - r_2\cos\gamma)\left\{\left(\frac{r_2}{r_3}\right)^{\frac{1}{2}}\frac{\Sigma_{15}}{\sqrt{2}} + \frac{1}{\sqrt{6}}\cdot\frac{1}{r_3}\Sigma_{14}\right\}\sin\gamma$$

$$- 2(r_2 - r_1\cos\gamma)\left\{\left(\frac{r_2}{r_3}\right)^{\frac{1}{2}}\frac{\Sigma_{25}}{\sqrt{2}} + \frac{1}{r_3}\frac{\Sigma_{24}}{\sqrt{6}}\right\}\sin\gamma\Big]$$

$$\sigma_{D^*} = (D^*)^{-2}\Big[(r_2 - r_3\cos\alpha)^2\Sigma_{22} + (r_3 - r_2\cos\alpha)^2\Sigma_{33}$$

$$+ \frac{2}{3}\frac{1}{r_1^2}\Sigma_{44}\sin^2\alpha + 2(r_2 - r_3\cos\alpha)(r_3 - r_2\cos\alpha)\Sigma_{23}$$

$$+ 2(r_2 - r_3 \cos \alpha) \frac{\sqrt{6}}{3r_1} \Sigma_{24} \sin \alpha$$

$$+ 2(r_3 - r_2 \cos \alpha) \frac{\sqrt{6}}{3r_1} \Sigma_{34} \sin \alpha \Big]$$

$$\sigma_{1^*} = (\mathrm{T}^*)^{-2} \Big[(r_3 - r_1 \cos \beta)^2 \Sigma_{33} + (r_1 - r_3 \cos \beta)^2 \Sigma_{11}$$

$$+ \left\{ \left(\frac{r_3}{r_2}\right) \frac{\Sigma_{55}}{2} + \frac{1}{6} \cdot \frac{1}{r_2^2} \Sigma_{44} - 2 \left(\frac{r_3}{r_2}\right)^{\frac{1}{2}} \frac{1}{\sqrt{12}\, r_2} \Sigma_{45} \right\} \sin^2 \beta$$

$$+ 2(r_3 - r_1 \cos \beta)(r_1 - r_3 \cos \beta) \Sigma_{13}$$

$$+ 2(r_3 - r_1 \cos \beta) \left\{ \left(\frac{r_3}{r_2}\right)^{\frac{1}{2}} \frac{\Sigma_{35}}{\sqrt{2}} - \frac{1}{\sqrt{6}} \frac{1}{r_2} \Sigma_{34} \right\} \sin \beta$$

$$+ 2(r_1 - r_3 \cos \beta) \left\{ \left(\frac{r_3}{r_2}\right)^{\frac{1}{2}} \frac{\Sigma_{15}}{\sqrt{2}} - \frac{1}{\sqrt{6}} \cdot \frac{1}{r_2} \Sigma_{14} \right\} \sin \beta$$

where,

$$\mathrm{R}^* = (r_1^2 + r_2^2 - 2r_1 r_2 \cos \gamma)^{\frac{1}{2}}$$

$$\mathrm{D}^* = (r_2^2 + r_3^2 - 2r_2 r_3 \cos \alpha)^{\frac{1}{2}}$$

and

$$\mathrm{T}^* = (r_3^2 + r_1^2 - 2r_1 r_3 \cos \beta)^{\frac{1}{2}}.$$

Similar expressions are derived for other additional mean-square amplitude values too.

4. Results

The elements of the matrix Σ are evaluated by solving the secular equation $|\Sigma \mathrm{G}^{-1} - \mathrm{E}\triangle| = 0$, where G^{-1} is the inverse kinetic energy matrix and E is the unit matrix. The values of $\triangle$ are connected with the normal frequency ν by the relation

$$\triangle = \frac{h}{8\pi^2 \nu} \coth\left(\frac{h\nu}{2k\mathrm{T}}\right)$$

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

The molecular parameters[4-7] and the observed frequencies[8-11] of linear and plane AXYZ type molecules are given in Tables I and II,

TABLE I

Molecular parameters and observed frequencies of HN_3, DN_3, HNCO and HNCS

Melecule	Molecular parameters				Observed frequencies (cm.$^{-1}$) A′				
	R Å	r_1 Å	r_2 Å	α	σ_1	σ_2	σ_3	σ_4	σ_5
HN_3 ..	1·021	1·240	1·134	112° 39′	3336	2140	1274	1150	522
DN_3 ..	1·021	1·240	1·134	112° 39′	2480	2141	1183	955	498
HNCO ..	0·987	1·207	1·171	128° 5′	3531	1327	2274	797	572
HNCS ..	1·013	1·216	1·561	130° 15′	3536	1963	860	817	469

TABLE II

Molecular parameters and observed frequencies of HCOF and DCOF

Molecule	Molecular parameters						Observed frequencies (cm.$^{-1}$) A′				
	r_1 Å	r_2 Å	r_3 Å	α	β	γ	σ_1	σ_2	σ_3	σ_4	σ_5
HCOF ..	1·10	1·34	1·18	122° 42′	129°	108°	2981	1837	1343	1065	663
DCOF ..	1·10	1·34	1·18	122° 42′	129°	108°	2262	1797	968	1073	658

The mean-square amplitudes of vibration and mean amplitudes of vibration are evaluated for bonded and non-bonded distances. The results obtained for the linear AXYZ molecules are given in Tables III and IV and those for the planar AXYZ molecules are given in Tables V and VI.

From the results presented in Tables III—VI the following conclusions may be drawn:

1. The N–H mean amplitude of vibration is the same in HN_3, HNCO and HNCS.

2. The N–N mean amplitude of vibration is found to be the same for the isotopic pair of molecules HN_3 and DN_3.

TABLE III

Mean-square amplitude quantities in Å² for NH_3, DN_3, HNCO and HNCS at 300° K.

Molecule / Symbol	HN_3	DN_3	HNCO	HNCS
σ_R ..	0·005526	0·004025	0·005503	0·005510
σ_{r_1} ..	0·001471	0·001478	0·001436	0·001412
σ_{r_2} ..	0·001266	0·001272	0·001226	0·001586
$\sigma_{r_1 r_2}$ ..	0·000156	0·000214	0·000251	0·000123
σ_α ..	0·015210	0·013360	0·025720	0·024890
σ_θ ..	0·016970	0·014410	0·013930	0·016470
$\sigma_{R\alpha}$ ..	0·000684	0·000651	0·000669	0·000649
σ_{Rr_1} ..	0·000767	0·000798	0·000786	0·000769
σ_{Rr_2} ..	0·000302	0·000321	0·000292	0·000313
$\sigma_{r_1\alpha}$ ..	0·000378	0·000366	0·000399	0·000447
$\sigma_{r_2\alpha}$ ..	0·000092	0·000093	0·000113	0·000147
σ_{R^*} ..	0·011190	0·009797	0·012170	0·012130
σ_{D^*} ..	0·014750	0·013360	0·016650	0·017020
σ_{RR^*} ..	0·005437	0·004251	0·005838	0·005887
σ_{RD^*} ..	0·005136	0·004163	0·005779	0·005812
$\sigma_{r_1 R^*}$ ..	0·002198	0·002069	0·002129	0·002708
$\sigma_{r_1 D^*}$ ..	0·002419	0·002409	0·002536	0·002136
$\sigma_{r_2 R^*}$ ..	−0·000431	−0·000495	−0·000590	−0·000473
$\sigma_{r_2 D^*}$ ..	−0·001644	−0·001679	−0·001854	−0·002010
$\sigma_{R^* D^*}$ ..	0·026260	0·025470	0·034150	0·036190

TABLE IV

Mean amplitudes (Å) for HN_3, DN_3, HNCO and HNCS at 300° K.

Molecule / Pair	HN_3	DN_3	HNCO	HNCS
A – X ..	0·07433	0·06345	0·07418	0·07423
X – Y ..	0·03835	0·03844	0·03789	0·03758
Y – Z ..	0·03558	0·03567	0·03501	0·03982
A...Y ..	0·10580	0·09901	0·11060	0·11010
A...Z ..	0·12140	0·11550	0·12900	0·13050

TABLE V

Mean-square amplitudes in $Å^2$ for HCOF and DCOF at 300° K.

Molecule / Symbol		HCOF	DCOF
σ_{r_1}	..	0·006304	0·004424
σ_{r_2}	..	0·001954	0·001959
σ_{r_3}	..	0·001310	0·001312
$\sigma_{r_1 r_2}$	..	0·000163	0·000155
$\sigma_{r_1 r_3}$	..	0·000154	0·000152
$\sigma_{r_2 r_3}$	..	0·000147	0·000138
σ_{α}	..	0·022500	0·019570
σ_{β}	..	0·015950	0·015545
σ_{γ}	..	0·016420	0·015975
σ_{R^*}	..	0·008002	0·006898
σ_{D^*}	..	0·004386	0·004365
σ_{T^*}	..	0·007649	0·006103
$\sigma_{r_1 R^*}$	..	0·004963	0·003519
$\sigma_{r_1 D^*}$	..	0·000278	0·000271
$\sigma_{r_1 T^*}$	..	0·005765	0·004106
$\sigma_{r_2 R^*}$	..	0·001784	0·001778
$\sigma_{r_2 D^*}$	..	0·001875	0·001873
$\sigma_{r_2 T^*}$	..	0·000279	0·000265
$\sigma_{r_3 R^*}$	..	0·000242	0·000260
$\sigma_{r_3 D^*}$	..	0·001261	0·001254
$\sigma_{r_3 T^*}$	..	0·001329	0·001332
$\sigma_{R^* D^*}$	..	0·000643	0·000745
$\sigma_{R^* D^*}$	..	0·003542	0·002287
$\sigma_{D^* T^*}$	..	0·000618	0·000686

TABLE VI

Mean amplitudes (Å) for HCOF and DCOF at 300° *K.*

Molecule / Pair	HCOF	DCOF
A – X ..	0·07939	0·06653
X – Y ..	0·03620	0·03622
X – Z ..	0·04421	0·04426
A...Z ..	0·08945	0·08307
Y...Z ..	0·06622	0·06607
A...Y ..	0·08746	0·07812

3. The C–N mean amplitude of vibration is very nearly the same in HNCO and HNCS.

4. The C–O and C–F mean amplitude values are the same for the isotopic molecules HCOF and DCOF.

ACKNOWLEDGMENT

One of the authors (V. M.) is thankful to the Council of Scientific and Industrial Research, Government of India, for the award of a Research Fellowship.

REFERENCES

1. Cyvin, S. J. .. *Acta Polytechnica Scand.*, 1960, Ph. **6**, 279.
2. Venkateswarlu, K. and Thirugnanasambandam, P. *Z. Phys. Chem.*, 1961, **1**, 218.
3. Thomas, W. J. O. .. *Dis. Farad. Soc.*, 1950, **9**, 339.
4. Amble, E. and Deiley, B. P. *J. Chem. Phys.*, 1950, **18**, 1422.
5. Jones, L. H., Shoolery, J. N., Shulman, R. G. and Don M. Yost. *Ibid.*, 1950, **18**, 990.
6. Dousmanis, G. C., Sanders, T. M., Jr., Towns, C. H. and Zeiger, H. J. *Ibid.*, 1953, **21**, 1416.

7. Le Blanc, O. H., Jr., Laurie, V. W. and Gwinn, W. D. *J. Chem. Phys.*, 1960, **33**, 598.

8. Dows, D. A. and Pimentel, G. C. *Ibid.*, 1955, **23**, 1258.

9. Herzberg, G. and Reid, C. *Dis. Farad. Soc.*, 1950, **9**, 92.

10. Morgan, H. W., Staats, P. A. and Goldstein, J. H. *J. Chem. Phys.*, 1956, **25**, 337.

11. Stratton, R. F. and Nielsen, A. H. *J. Mol. Spectroscopy*, 1960, **4**, 373.