MEAN AMPLITUDES OF VIBRATION : BENT SYMMETRICAL XY_2 MOLECULES AND GROUPS

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ABSTRACT

Applying the secular equation method of Cyvin, the mean-square amplitudes and the mean amplitudes for ten bent symmetrical XY_2 molecules and groups at 300° K. have been evaluated.

INTRODUCTION

THE bent symmetrical XY_2 molecules belong to the point group C_{2v} and possess $2a_1 + 1b_1$ types of vibration.

The following orthonormal set of symmetry co-ordinates is formed using the valence force co-ordinates r_1, r_2 and α representing the deviations from equilibrium values (Fig. 1).

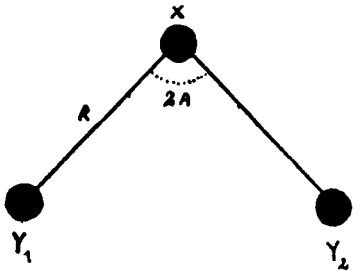

FIG. 1.

For the a_1 type:

$$S_1 = 2^{-\frac{1}{2}} (r_1 + r_2)$$
$$S_2 = R\alpha. \qquad (1)$$

For the b_1 type:

$$S_3 = 2^{-\frac{1}{2}} (r_1 - r_2)$$

Here the angle displacement co-ordinate is multiplied by the equilibrium bond length R.

SYMMETRIZED MEAN-SQUARE AMPLITUDE MATRIX

The quantities of the symmetrized mean-square amplitude matrix Σ in terms of the symmetry co-ordinates are given below:

$$\Sigma_{11} = \langle S_1^2 \rangle = (\sigma + \sigma')$$
$$\Sigma_{12} = \langle S_1 S_2 \rangle = 2^{\frac{1}{2}} \rho$$
$$\Sigma_{22} = \langle S_2^2 \rangle = \tau$$
$$\Sigma_{33} = \langle S_3^2 \rangle = (\sigma - \sigma'). \qquad (2)$$

The various mean-square amplitudes and interaction mean-square amplitudes appearing in equations (2) can be defined as follows:

$$\sigma = \langle r_1^2 \rangle = \langle r_2^2 \rangle \qquad \sigma' = \langle r_1 r_2 \rangle$$
$$\tau = R^2 \langle \alpha^2 \rangle \qquad \rho = R \langle r_1 \alpha \rangle = R \langle r_2 \alpha \rangle, \qquad (3)$$

Considering the nonbonded distance deviations r^*, the following additional mean-square amplitude quantities are obtained in terms of the quantities in equations (3). They are

$$\sigma^* = \langle (r^*)^2 \rangle = 2(\sigma + \sigma') \sin^2 A + \tau \cos^2 A + 2\rho \sin 2A$$
$$\sigma'^* = \langle r r^* \rangle = (\sigma + \sigma') \sin A + \rho \cos A$$

where 2A is the interbond angle.

KINETIC ENERGY MATRIX G

Using Wilson's[1] method, the following elements of the G-matrix are obtained:

$$G_{11} = 2\mu_X \cos^2 A + \mu_Y$$
$$G_{12} = -2^{\frac{1}{2}} \mu_X \sin 2A$$
$$G_{22} = 2(2\mu_X \sin^2 A + \mu_Y)$$
$$G_{33} = 2\mu_X \sin^2 A + \mu_Y$$

where μ_X and μ_Y denote the reciprocal masses of the X and Y atoms respectively.

RESULTS

The elements of the mean-square amplitude matrix Σ are obtained by solving the secular equation[2]

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

where G^{-1} is the inverse of the kinetic energy matrix and the values of $\triangle$ are given by the equation

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

Here ν_k is the normal frequency, h Planck's constant, k Boltzmann's constant and T the absolute temperature.

The observed fundamental frequencies and interbond angles of the molecules and groups studied in this investigation are given in Table I.

TABLE I

Interbond angles and observed frequencies ($cm.^{-1}$) of some bent symmetrical XY_2 molecules and groups

Molecule or Group	Interbond angle 2A	Observed frequencies ($cm.^{-1}$)			Reference
		a_1		b_1	
		ν_1	ν_2	ν_3	
H_2S	92°	2615	1183	2627	(3)
D_2S	92°	1892	934	2000	(4)
H_2Se	91°	2260	1074	2350	(5)
D_2Se	91°	1630	745	1696	(5)
SO_2	119° 32′	1151	518	1362	(6)
F_2O	101° 30′	929	461	826	(7)
Cl_2O	111° 8′	688	320	969	(8)
CCl_2	112°	700	284	738	(9)
CBr_2	112°	576	175	640	(9)
CI_2	114° 42′	485	120	567	(9)

The elements of the Σ matrix evaluated from the vibrational frequencies and the elements of the inverse kinetic energy matrix are given in Table II for the cases studied here.

TABLE II

Symmetrized mean-square amplitude matrices in $A^{\circ 2}$ for some bent symmetrical XY_2 molecules and groups at 300° K.

Molecule or Group \ Element	Σ_{11}	Σ_{12}	Σ_{22}	Σ_{33}
H_2S	0·006603	−0·000821	0·029356	0·006564
D_2S	0·004668	−0·000520	0·019511	0·004445
H_2Se	0·008381	−0·002358	0·035489	0·008017
D_2Se	0·006319	−0·001425	0·029120	0·006201
SO_2	0·001215	−0·001042	0·008268	0·001352
F_2O	0·002095	−0·000921	0·007956	0·002702
Cl_2O	0·001862	−0·001524	0·011209	0·002009
CCl_2	0·002342	−0·001060	0·011819	0·003450
CBr_2	0·002823	−0·001710	0·013800	0·003672
CI_2	0·002984	−0·002030	0·021399	0·004270

The most important ones of the mean-square amplitude quantities are σ and σ^* representing the mean-square amplitudes of vibration for the bonded and non-bonded distances respectively. They are listed in Table III along with the mean amplitude quantities $\sigma^{\frac{1}{2}}$ and $(\sigma^*)^{\frac{1}{2}}$ for the bonded and non-bonded distances respectively.

The above results are useful

(i) in the interpretation of the electron diffraction data;

(ii) in providing an additional set of parameters required in defining the non-rigid model of the molecules;

(iii) in giving additional information to normal frequencies in the determination of a complete harmonic force field.

TABLE III

Mean-square amplitudes ($A^{\circ 2}$) *and mean amplitudes* (A°) *for some bent symmetrical* XY_2 *molecules and groups at* 300° *K.*

Molecule or Group \ Symbol	Mean-square amplitude ($A^{\circ 2}$)		Mean amplitude (A°)	
	(X—Y)	(Y—··Y)	(X—Y)	(Y···Y)
	σ	σ^*	$\sigma^{\frac{1}{2}}$	$(\sigma^*)^{\frac{1}{2}}$
H_2S	0·006584	0·019840	0·081142	0·140855
D_2S	0·004568	0·013511	0·067513	0·116237
H_2Se	0·008199	0·022631	0·090548	0·150390
D_2Se	0·006260	0·018722	0·079120	0·136829
SO_2	0·001284	0·002616	0·035834	0·051144
F_2O	0·002399	0·003893	0·048980	0·062394
Cl_2O	0·001936	0·004611	0·044001	0·067905
CCl_2	0·002896	0·005527	0·053815	0·074336
CBr_2	0·003248	0·005956	0·056990	0·077170
CI_2	0·003627	0·007886	0·060221	0·088798

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