GENERALISED MEAN SQUARE AMPLITUDES AND CORIOLIS COUPLING COEFFICIENTS OF METHYLENE HALIDES

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The generalised mean square amplitudes of vibration for both bonded and nonbonded atom pairs and the Coriolis coupling coefficients have been evaluated for the molecules CH_2F_2, CH_2Cl_2, CH_2Br_2 and CH_2I_2. The ζ values indicate that there is very strong Coriolis coupling between the CH_2 symmetric deformation and the $D-H$ asymmetric stretching vibrations. The results are discussed in relation to the structure of the molecules.

1. Introduction

The vibrational spectra of methylene halides have been investigated and normal coordinate analyses have been carried out by some earlier investigators [1–5]. Though the parallel mean amplitudes of vibration of similar type of molecules have been determined by Venkateswarlu *et al.* [6], the generalised mean square amplitudes of vibration of these molecules have not been studied so far. No attempt has been made hitherto to evaluate the Coriolis coupling constants of XY_2Z_2 type of molecules. In the present investigation the generalised mean square amplitudes and Coriolis coupling coefficients of these molecules are obtained.

These molecules belong to the symmetry point group C_{2v} with the vibrations distributed among $4a_1+1a_2+2b_1+2b_2$ normal modes. All the nine vibrations are active in Raman spectrum while all the fundamentals except a_2 are infrared active.

2. Generalised mean square amplitudes

The symmetrized mean square amplitudes Σ are obtained from the relation [7]

$$\sum = L\,\Delta\tilde{L}$$

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where L represents the normal co-ordinate transformation matrix and Δ is a diagonal matrix with elements [8]

$$\Delta_i = \frac{h}{8\pi^2 \nu_i} \operatorname{Coth}\left(\frac{h\nu_i}{2kT}\right)$$

the symbols are having their usual significance. The generalised mean square amplitudes, namely the mean square parallel amplitude $\langle(\Delta z)^2\rangle$ the mean square perpendicular amplitudes $\langle(\Delta x)^2\rangle$, $\langle(\Delta y)^2\rangle$ and the mean cross products $\langle(\Delta z)\cdot(\Delta x)\rangle$, $\langle(\Delta x)\cdot(\Delta y)\rangle$, $\langle(\Delta y)\cdot(\Delta z)\rangle$ [9] have been evaluated for both bonded and non bonded atom pairs and are presented in Table I.

TABLE I

Generalised mean square amplitudes of methylene halides (at 300°K) in 10^{-4} Å^2

Molecule	Atom pair	Distance Å	$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$	$\langle(\Delta z).(\Delta x)\rangle$	$\langle\Delta x).(\Delta y)\rangle$	$\langle(\Delta y).(\Delta z)\rangle$
CH_2F_2	C—F	1.358	22.75	23.49	6.55	9.50	0	0
	C—H	1.093	52.99	135.15	121.47	0	0	16.98
	F...F	2.218	61.85	2.53	0.47	0	0	0
	H...H	1.784	172.99	257.66	184.80	0	0	0
	F...H	2.007	127.35	136.66	62.36	−16.85	−11.20	8.17
CH_2Cl_2	C—Cl	1.772	25.10	39.46	5.66	−4.01	0	0
	C—H	1.082	59.54	150.58	153.42	0	0	−5.95
	Cl...Cl	2.895	28.22	1.22	0	0	0	0
	H...H	1.767	153.60	289.70	262.36	0	0	0
	Cl...H	2.364	159.54	164.92	58.38	8.29	−11.93	18.66
CH_2Br_2	C—Br	1.907	26.80	43.18	53.72	0.56	0	0
	C—H	1.093	60.31	159.80	168.97	0	0	−4.73
	Br...Br	3.115	41.62	0.34	0	0	0	0
	H...H	1.784	167.02	307.10	294.92	0	0	0
	Br...H	2.495	160.63	173.91	64.51	0.73	−26.57	9.11
CH_2I_2	C—I	2.120	30.87	44.63	5.47	1.39	0	0
	C—H	1.093	61.39	171.22	190.85	0	0	2.33
	I...I	3.462	43.81	0.16	0	0	0	0
	H...H	1.784	169.10	327.50	342.29	0	0	0
	I...H	2.689	181.84	191.66	66.60	7.49	−32.55	7.96

3. *Coriolis coupling coefficients*

The Coriolis matrices are obtained from the relation

$$C_{ij}^{\alpha} = \sum_{p} \sum_{p} \mu\,(S_i^p \times S_j^p)\cdot e_{\alpha}$$

where 'S's are Wilson's vectors for the atom p; μ_p is its reciprocal mass and e_α is a unit vector in the α direction. The C matrix elements for XY_2Z_2 type of molecules are given by

$$C^z_{1,5} = \frac{1}{\sqrt{2}}\left[\varrho\mu_z - \frac{\mu_y}{\varrho}\right]; \qquad \varrho = \left(\frac{R}{r}\right)^{1/2}$$

$$C^z_{2,5} = -\frac{1}{\sqrt{2}}\left[\varrho\mu_z + \frac{\mu_y}{\varrho}\right]$$

$$C^z_{3,5} = -\frac{1}{\sqrt{2}}\left[\varrho\mu_z + \frac{\mu_y}{\varrho}\right]$$

$$C^z_{4,5} = \frac{1}{\sqrt{3}}\varrho\mu_z\left[1+\frac{\varrho}{2}\right] - \frac{1}{\sqrt{3}}\frac{\mu_y}{\varrho}\left[1+\frac{1}{2\varrho}\right]$$

$$C^z_{6,8} = \frac{4}{3}\mu_x$$

$$C^z_{6,9} = \varrho\mu_z + 2\mu_x\left[\varrho + \frac{1}{3\varrho}\right]$$

$$C^z_{7,8} = \frac{\mu_y}{\varrho} + 2\mu_x\left[\frac{\varrho}{3} + \frac{1}{\varrho}\right]$$

$$C^z_{7,9} = \frac{\varrho^2\mu_z}{2} + \frac{\mu_y}{2\varrho^2} + \frac{\mu_x}{3}\left[10 + 3\varrho^2 + \frac{3}{\varrho^2}\right]$$

$$C^y_{1,6} = 0$$

$$C^y_{1,7} = \frac{\mu_y}{2\varrho} - \frac{\varrho}{2}\mu_z$$

$$C^y_{2,6} = \frac{4}{3}\mu_x$$

$$C^y_{2,7} = \frac{\varrho\mu_z}{2} + \frac{\mu_y}{2\varrho} + 2\mu_x\left[\frac{\varrho}{3} + \frac{1}{\varrho}\right]$$

$$C^y_{3,6} = -\mu_z - \frac{8}{3}\mu_x$$

$$C^y_{3,7} = -\frac{\mu_y}{\varrho} - 4\mu_x\left[\frac{\varrho}{3} + \frac{1}{\varrho}\right]$$

$$C^y_{4,6} = \frac{\mu_z}{\sqrt{6}}[\varrho+2] + \frac{4}{3\sqrt{6}}\mu_x\left[\varrho - \frac{1}{\varrho}\right]$$

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$$C^{y}_{4,7} = -\frac{\mu_y}{\sqrt{6}}\left[\frac{1}{\varrho^2} + \frac{2}{\varrho}\right] + \frac{2}{\sqrt{6}}\mu_x\left[\frac{\varrho^2}{3} + \frac{2}{3} - \frac{1}{\varrho^2}\right]$$

$$C^{y}_{5,8} = -\frac{1}{\sqrt{2}}\frac{\mu_y}{\varrho}$$

$$C^{y}_{5,9} = \frac{1}{\sqrt{2}}\frac{\mu_y}{\varrho^2}$$

$$C^{x}_{1,8} = 0$$

$$C^{x}_{1,9} = \frac{\varrho\mu_z}{2} - \frac{\mu_y}{2\varrho}$$

$$C^{x}_{2,8} = -\frac{4}{3}\mu_x$$

$$C^{x}_{2,9} = -\frac{\varrho\mu_z}{2} - \frac{\mu_y}{2\varrho} - 2\mu_x\left[\varrho + \frac{1}{3\varrho}\right]$$

$$C^{x}_{3,8} = \mu_y + \frac{8}{3}\mu_x$$

$$C^{x}_{3,9} = \varrho\mu_z + 4\mu_x\left[\varrho + \frac{1}{3\varrho}\right]$$

$$C^{x}_{4,8} = \frac{\mu_y}{\sqrt{6}}\left[2 + \frac{1}{\varrho}\right] - \frac{4}{3\sqrt{6}}\mu_x\left[\varrho - \frac{1}{\varrho}\right]$$

$$C^{x}_{4,9} = -\frac{\mu_z}{\sqrt{6}}\left[\varrho^2 + 2\varrho\right] - \frac{2}{\sqrt{6}}\mu_x\left[\varrho^2 - \frac{2}{3} - \frac{1}{3\varrho^2}\right]$$

$$C^{x}_{5,6} = -\frac{\varrho\mu_z}{\sqrt{2}}$$

$$C^{x}_{5,7} = \frac{\varrho^2\mu_z}{\sqrt{2}}\,.$$

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The Coriolis coupling coefficients are evaluated by the method of Meal and Polo [10]

$$\zeta^{\alpha} = L^{-1} C^{\alpha} (\tilde{L})^{-1}.$$

For XY_2Z_2 type of molecules, by Jahn's rule (11) the following Coriolis couplings are found to be nonvanishing

$a_1 \times b_2$ and $a_2 \times b_1$ corresponding to ζ^x

$a_1 \times b_1$ and $a_2 \times b_2$ corresponding to ζ^y

$a_1 \times a_2$ and $b_1 \times b_2$ corresponding to ζ^z.

The values of the Coriolis coupling coefficients are given in Tables II, III and IV.

TABLE II

ζ^x values of methylene halides

Zeta elements	CH_2F_2	CH_2Cl_2	CH_2Br_2	CH_2I_2
$a_1 \times b_2$				
$\zeta_{1,8}$	0.0274	−0.0234	−0.0469	−0.0450
$\zeta_{1,9}$	−0.8771	−0.9335	−0.9312	−0.9463
$\zeta_{2,8}$	0.1464	0.0612	0.0216	0.0703
$\zeta_{2,9}$	−0.4205	−0.3670	−0.3451	−0.3156
$\zeta_{3,8}$	0.9904	0.9975	1.0000	1.0000
$\zeta_{3,9}$	0.0921	0.0034	−0.0357	−0.0198
$\zeta_{4,8}$	0.0248	0.0228	0.0203	0.0233
$\zeta_{4,9}$	−0.2262	−0.1439	−0.0869	−0.0450
$a_2 \times b_1$				
$\zeta_{5,6}$	−0.0705	−0.0311	−0.0138	−0.0079
$\zeta_{5,7}$	−0.0092	0.0022	0.0013	0.0009

TABLE III

ζ^y values of methylene halides

Zeta elements	CH_2F_2	CH_2Cl_2	CH_2Br_2	CH_2I_2
$a_1 \times b_1$				
$\zeta_{1,6}$	−0.2164	−0.1038	−0.0805	−0.0488
$\zeta_{1,7}$	0.4916	0.5760	0.5934	0.5876
$\zeta_{2,6}$	0.5715	0.7442	0.8486	0.9294
$\zeta_{2,7}$	0.2203	0.1139	0.1036	−0.0182
$\zeta_{3,6}$	0.2334	0.0515	0.0522	−0.0204
$\zeta_{3,7}$	−0.8065	−0.8146	−0.8006	−0.8039
$\zeta_{4,6}$	0.7299	0.6584	0.4318	0.2591
$\zeta_{4,7}$	0.2172	0.0218	−0.0054	0.0599
$a_2 \times b_2$				
$\zeta_{5,8}$	−0.5586	−0.5566	−0.5610	−0.5649
$\zeta_{5,9}$	0.7087	0.7660	0.7769	0.7852

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TABLE IV

ζ^z values of methylene halides

Zeta elements	CH_2F_2	CH_2Cl_2	CH_2Br_2	CH_2I_2
$a_1 \times a_2$				
$\zeta_{1,5}$	−0.8222	−0.8233	−0.7973	−0.7971
$\zeta_{2,5}$	−0.1729	−0.1016	−0.0560	−0.0685
$\zeta_{3,5}$	−0.5204	−0.5732	−0.6019	−0.6016
$\zeta_{4,5}$	0.1455	0.0860	0.0421	0.0288
$b_1 \times b_2$				
$\zeta_{6,8}$	−0.3248	−0.1143	−0.0815	−0.0528
$\zeta_{6,9}$	0.2031	0.2762	0.2756	0.3226
$\zeta_{7,8}$	0.7450	0.8193	0.8225	0.8199
$\zeta_{7,9}$	0.6480	0.5696	0.5611	0.5579

4. *Results and discussion*

It is found that the generalized mean square amplitudes of C-Halogen and H... Halogen atom pairs increase with the higher members of the halogen group, that is, as the electronegativity of the atom decreases. Also it is seen that both the mean square parallel and perpendicular amplitudes of vibration of the C–H bond increase with higher halogen substitutions. In all cases the mean square perpendicular amplitude $\langle(\Delta y)^2\rangle$ of the C-Halogen bond is found to be extremely small. The mean square perpendicular amplitudes $\langle(\Delta x)^2\rangle$ and $\langle(\Delta y)^2\rangle$ of the C–H bond are very nearly equal. The H...H mean square amplitude in CH_2Cl_2 is slightly smaller than that in the other molecules. This may be due to the slightly smaller value of the H...H distance in CH_2Cl_2 than in the other molecules.

The Coriolis coefficients $\zeta^z_{1,5}$ arising from $a_1 \times a_2$ coupling and $\zeta^z_{7,8}$ arising from $b_1 \times b_2$ coupling are rather large indicating that the corresponding coupling are very strong. But with higher halogen substitutions $\zeta^z_{1,5}$ decreases while $\zeta^z_{7,8}$ increases. The $\zeta^x_{3,8}$'s due to the $a_1 \times b_2$ coupling are very close to unity suggesting that the Coriolis coupling between the CH_2 symmetric deformation and the asymmetric C–H stretching vibrations is very strong. The coupling between a_2 and b_1 vibrations is found to be very weak. It is seen that $\zeta^y_{3,7}$ arising from $a_1 \times b_1$ coupling has high magnitude and its value remains more or less unaltered with halogen substitution.

The generalised mean square amplitudes and the Coriolis coupling constants are useful in electron diffraction analysis and in vibration-rotation interaction studies.

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