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MEAN AMPLITUDES, CORIOLIS COUPLING CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF SOME PYRAMIDAL XY_3 HALIDES

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The mean amplitudes of vibration, the Coriolis coupling constants and the centrifugal distortion constants of eight pyramidal XY_3 halides have been studied with the help of kinetic constants. The values of these molecular constants seem to be reasonable and also in good agreement with the literature values.

1. Introduction

Wilson's F–G matrix method, coupled with kinetic constants and redundancy constraints has been found to lead to acceptable sets of molecular constants in several molecular types [1–8]. Extending this new procedure to pyramidal XY_3 molecules, the molecular kinetic constants, the force constants and the mean amplitudes have been reported for Group V hydrides and some halides [4–8].

The purpose of the present paper is to test the validity of the force field by calculating the other molecular constants viz., mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants. The values of these molecular constants are in good agreement with the observed values, showing the significance of the procedure adopted in the present study.

2. Theoretical considerations

The kinetic constants and the force constants of the XY_3 (C_{3v}) pyramidal type (X = P, As; Y = F, Cl, Br, I) have already been reported by the author [8]. The theory adopted, closely follows the details given in the earlier paper [4]. Utilising these force constants

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in Cyvin's secular equation [9], the symmetrized mean square amplitude elements and hence the mean amplitudes are obtained.

The Coriolis matrix elements $C^{\alpha}_{ij}(\alpha = x, y, z)$ are obtained by the vector method of Meal and Polo [10] and the zeta matrix elements are evaluated from the relation $\zeta^{\alpha} = L^{-1}C^{\alpha}(L')^{-1}$ making use of the kinetic constants.

Cyvin et al. [11] have formulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta}$'s instead of partial derivatives of the inertia tensor components $J_{\alpha\beta}$'s of Kivelson and Wilson [12, 13]. The quantities $t_{\alpha\beta\gamma\delta}$ have been obtained using Cyvin's relation and the nonvanishing $T_{\alpha\beta}$'s matrix elements have been evaluated. The centrifugal distortion constants of these eight molecules have been calculated using the force constants given by the author [8].

3. *Results and discussion*

Results related to eight pyramidal XY_3 halides are discussed here. The valence mean square amplitudes and the mean amplitudes are given in Tables I and II, respectively. The values of the mean amplitudes for both the bonded and the non-bonded distances of the pyramidal halides appear to be reasonable. The mean amplitudes of vibration evaluated in the present investigation compare favourably with the published data wherever such results are available. The mean amplitudes $\sigma_d^{1/2}$ and $\sigma_q^{1/2}$ corresponding to the bonded and the non-bonded distances respectively, are found to increase with the decrease of electronegativity in the case of Y atoms which is the reverse in the case of force constants. The present set of values will be useful in the interpretation of electron diffraction data related to these molecules.

Tables III and IV deal with calculated values of the Coriolis coupling constants and the centrifugal distortion constants of phosphorus and arsenic halides. The zeta values in Table III may be seen to obey the following sum rules given by Oka [14].

$$(\zeta^{y}_{1a3a})^2+(\zeta^{y}_{1a4a})^2+(\zeta^{y}_{2a3a})^2+(\zeta^{y}_{2a4a})^2+(\zeta^{y}_{3a4a})^2 = 1,$$

$$2[(\zeta^{y}_{1a3a})^2+(\zeta^{y}_{1a4a})^2+(\zeta^{y}_{2a3a})^2+(\zeta^{y}_{2a4a})^2-\tfrac{1}{2}]-(\zeta^{z}_{3a4b})+(\zeta^{z}_{3a3b})(\zeta^{z}_{4a4b}) = 0.$$

They also further obey the relation

$$(\zeta^{y}_{1a3a})(\zeta^{y}_{2a4a})-(\zeta^{y}_{1a4a})(\zeta^{y}_{2a3a}) = 0.$$

The magnitude of ζ^{z}_{3a3b} and ζ^{y}_{1a3a} are of the same order except in the case of PI_3 and PBr_3. The Coriolis coupling constants and the centrifugal distortion constants obtained here are compared with the values of the earlier workers and good agreement between the present values and the observed values has been noticed. Uniform trends have also been seen in the values of the molecular constants of these molecules.

TABLE I

Mean square amplitudes (10^{-3} Å^2) at 298.16 K

Molecule	σ_d σ_{dd}	σ_α $\sigma_{\alpha\alpha}$ $\sigma'_{d\alpha}$ $\sigma''_{d\alpha}$	σ_q σ_{qq} σ'_{dq} σ''_{dq}
PF_3	1.6959	9.9539	5.1524
	−0.1330	−1.1212	−0.0902
		0.2834	−0.0838
		−0.6289	0.7929
PCl_3	2.5289	17.0401	6.6249
	−0.2862	−0.5694	0.0914
		0.6214	−0.0463
		−1.3066	0.8995
PBr_3	2.6015	25.6688	8.4910
	−0.5168	−2.4001	−0.5208
		1.3716	0.00001
		−1.8022	0.5803
PI_3	3.2761	34.8257	12.0084
	−0.4454	−0.6946	−0.6288
		1.1636	−0.0401
		−2.6594	0.5262
AsF_3	1.5796	13.3536	6.9056
	−0.0813	−1.6658	−0.1073
		0.1217	−0.0422
		−0.3276	0.9781
$AsCl_3$	2.4241	21.4879	10.2616
	−0.1857	−1.8941	−0.1711
		0.3093	−0.0804
		−0.7447	1.2065
$AsBr_3$	2.3868	25.2950	11.5347
	−0.3047	−1.9099	−0.4321
		0.6651	−0.0305
		1.3441	
AsI_3	3.7368	31.7168	10.5062
	−0.6489	−1.9184	−1.9201
		3.3803	−0.1463
		−0.1767	0.2244

On the whole, it is thus seen that the kinetic constants do play a fundamental role in molecular dynamics and a recognition of the same leads to acceptable sets of molecular constants.

TABLE II

Mean amplitudes (Å)

Molecule	$\sigma_d^{\frac{1}{2}}$	$\sigma_q^{\frac{1}{2}}$
PF_3	0.0412	0.0712
PCl_3	0.0503	0.0814
PBr_3	0.0510	0.0922
PI_3	0.0572	0.1096
AsF_3	0.0397	0.0831
$AsCl_3$	0.0492	0.1013
$AsBr_3$	0.0488	0.1074
AsI_3	0.0611	0.1025

TABLE III

Coriolis coupling constants

Molecule	ζ^z_{3a3b}	$-\zeta^z_{4a4b}$	ζ^z_{3a4b}	$-\zeta^y_{1a3a}$	$-\zeta^y_{1a4a}$	ζ^y_{2a3a}	ζ^y_{2a4a}	ζ^y_{3a4a}
PF_3	0.4071	0.5999	0.7504	0.3598	0.1918	0.7577	0.4040	0.3105
PCl_3	0.5703	0.6821	0.7066	0.4911	0.2210	0.7375	0.3319	0.2365
PBr_3	0.7647	0.8038	0.5884	0.6387	0.2130	0.6888	0.2296	0.1398
PI_3	0.2021	0.2372	0.9576	0.7660	0.2046	0.5738	0.1546	0.1325
AsF_3	0.2239	0.4887	0.7911	0.1862	0.1203	0.7599	0.4911	0.3627
$AsCl_3$	0.3481	0.5533	0.7763	0.2942	0.1693	0.7666	0.4413	0.3200
$AsBr_3$	0.5540	0.6690	0.7173	0.4717	0.2176	0.7448	0.3437	0.2392
AsI_3	0.6685	0.7469	0.6495	0.5848	0.2276	0.7016	0.2731	0.1988

TABLE IV

Centrifugal distortion constants (KHz)

Molecule	D_J	$-D_{JK}$	D_K
PF_3	7.694	11.651	5.331
PCl_3	1.101	1.800	0.839
PBr_3	0.182	0.314	0.147
PI_3	0.067	0.115	0.053
AsF_3	4.693	6.600	3.166
$AsCl_3$	0.748	1.099	0.522
$AsBr_3$	0.150	0.244	0.109
AsI_3	0.045	0.078	−0.031

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