MEAN AMPLITUDES OF VIBRATION: SOME PYRAMIDAL XY_3 AND TETRAHEDRAL XY_4 MOLECULES

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Abstract

The theory of the determination of the mean amplitudes of vibration in molecules using the symmetry co-ordinates has been applied to the cases of arsenic halides belonging to the pyramidal XY_3 type and a few silicon and stannic halides of the tetrahedral XY_4 type. The mean square amplitudes and mean amplitudes of vibration have been evaluated at 298° K.

Introduction

The pyramidal XY_3 molecules have the symmetry C_{3v} and possess $2a_1 + 2e$ types of vibration. The orthonormal set of symmetry co-ordinates used for these molecules is the same as that given by Sundaram.[1]

The tetrahedral XY_4 molecules belong to the point group T_d and have $1a_1 + 1e + 2f_2$ vibrations. The symmetry co-ordinates made use of for this type are the same as those given by Cyvin.[2] The F and G matrices for the most general harmonic potential function have been worked out for the pyramidal XY_3 and tetrahedral XY_4 molecules by Sundaram[3] and Pistorius[4] respectively. While computing the matrix elements in the present case, proper account of the equilibrium bond length R has been taken.

Mean Square Amplitude Matrix

The elements of the symmetrized mean square amplitude matrix Σ are related to the mean square amplitude quantities σ in the following way:

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Pyramidal XY_3 type:

$$\Sigma_1 = \sigma_r + 2\sigma_{rr} \qquad \Sigma_{12} = \sigma_{r\alpha} + \sigma_{r\alpha'}$$
$$\Sigma_2 = \sigma_\alpha + 2\sigma_{\alpha\alpha}$$
$$\Sigma_3 = \sigma_r - \sigma_{rr} \qquad \Sigma_{34} = \sigma_{r\alpha} - \sigma_{r\alpha'} \qquad (1)$$
$$\Sigma_4 = \sigma_\alpha - \sigma_{\alpha\alpha}$$

Tetrahedral XY_4 type:

$$\Sigma_1 = \sigma_r + 3\sigma_{rr} \qquad \Sigma_2 = \sigma_\alpha - 2\sigma_{\alpha\alpha} + \sigma_{\alpha\alpha'}$$
$$\Sigma_3 = \sigma_r - \sigma_{rr} \qquad \Sigma_{34} = 2^{1/2}(\sigma_{r\alpha} - \sigma_{r\alpha'}) \qquad (2)$$
$$\Sigma_4 = \sigma_\alpha - \sigma_{\alpha\alpha'}.$$

In equations (1) and (2) the entering quantities are defined by the mean values given in the following:

$$\sigma_r = \langle r_1^2 \rangle; \quad \sigma_{rr} = \langle r_1 r_2 \rangle; \quad \sigma_\alpha = R^2 \langle \alpha_{12}^2 \rangle;$$
$$\sigma_{\alpha\alpha} = R^2 \langle \alpha_{12}\alpha_{23} \rangle; \quad \sigma_{\alpha\alpha'} = R^2 \langle \alpha_{12}\alpha_{34} \rangle;$$
$$\sigma_{r\alpha} = R \langle r_1 \alpha_{12} \rangle; \quad \sigma_{r\alpha'} = R \langle r_1 \alpha_{23} \rangle;$$

where r is the change in bond length, R the equilibrium bond length and α the change in bond angle. In the case of tetrahedral XY_4 molecules, some linear combinations of the above mean square amplitude quantities are equal to zero due to redundancy.

From the well-known relations:

$$\langle S_r^2 \rangle = 0; \quad \langle S_r S_i \rangle = 0$$

where S_r is the redundant co-ordinate and S_i an arbitrary co-ordinate, it is found that

$$\sigma_\alpha + 4\sigma_{\alpha\alpha} + \sigma_{\alpha\alpha'} = 0; \quad \sigma_{r\alpha} + \sigma_{r\alpha'} = 0.$$

Additional Mean Square Amplitude Matrices

When the interatomic displacements 'd_{ik}' between non-bonded pairs of atoms are considered, additional mean square amplitude quantities must be taken into account. The following quantities are introduced:

$$\sigma_d = \langle d_{12}^2 \rangle; \quad \sigma_{dd} = \langle d_{12} d_{23} \rangle; \quad \sigma_{dd'} = \langle d_{12} d_{34} \rangle$$
$$\sigma_{rd} = \langle r_1 d_{12} \rangle; \quad \sigma_{rd'} = \langle r_1 d_{23} \rangle.$$

All the above quantities may be expressed in terms of the symmetrized mean square amplitude matrix elements[1, 2] Σ.

NORMAL FREQUENCIES

The elements of the matrix Σ are evaluated by solving the secular equation

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

where G is the kinetic energy matrix and $\triangle$ is related to the normal frequency ν as

$$\triangle i = \left(\frac{h}{8\pi^2 \nu_i}\right) \coth\left(\frac{h\nu_i}{2kT}\right)$$

where h is Planck's constant, k Boltzmann's constant and T the temperature in degrees Kelvin.

RESULTS

The vibrational frequencies for the pyramidal XY_3 and tetrahedral XY_4 molecules studied here have been taken from Landolt-Börnstein Tables.[5]

The matrix elements Σ are evaluated from the vibrational frequencies and the elements of the inverse kinetic energy matrix. The results obtained for the pyramidal XY_3 molecules are given in Tables I to III and those for the tetrahedral XY_4 molecules are listed in Tables IV to VI.

TABLE I

Symmetrized mean square amplitude matrices in Å² for AsF_3, $AsCl_3$ and $AsBr_3$

Element \ Molecule		AsF_3	$AsCl_3$	$AsBr_3$
Σ_1	..	0·003532	0·003681	0·003805
Σ_{12}	..	0·000813	0·001630	0·0007
Σ_2	..	0·004583	0·008849	0·01241
Σ_3	..	0·006125	0·007374	0·008624
Σ_{34}	..	0·001392	0·00345	0·002516
Σ_4..	..	0·004607	0·01081	0·01514

TABLE II

Mean square amplitude quantities in Å² for AsF_3, $AsCl_3$ and $AsBr_3$ at 298° K.

Molecule / Symbol		AsF_3	$AsCl_3$	$AsBr_3$
σ_r	..	0·005260	0·006143	0·007017
σ_{rr}	..	−0·000864	−0·001230	−0·001607
σ_α	..	0·005113	0·010156	0·014230
$\sigma_{\alpha\alpha}$	..	0·000506	−0·000654	−0·000910
$\sigma_{r\alpha}$	..	0·000735	0·001694	0·001072
$\sigma_{r\alpha'}$	..	−0·000657	−0·001756	−0·001444
σ_δ	..	0·008413	0·013252	0·014351
$\sigma_{\delta\delta}$	..	0·001641	0·000587	0·000785
$\sigma_{r\delta}$	..	0·003779	0·004899	0·004846
$\sigma_{r\delta'}$	..	−0·001730	−0·002593	0·003440

TABLE III

Mean square amplitudes and mean amplitudes of AsF_3, $AsCl_3$ and $AsBr_3$

Molecule	Pair	Mean square amplitude Å²	Mean amplitude Å
AsF_3	As – F	0·005260	0·07252
	F ··· F	0·008413	0·09173
$AsCl_3$	As – Cl	0·006143	0·07838
	Cl ··· Cl	0·013252	0·11510
$AsBr_3$	As — Br	0·007017	0·08375
	Br ··· Br	0·014351	0·11980

TABLE IV

Symmetrized mean square amplitude matrices in Å² for $SiCl_4$, $SiBr_4$, $SnCl_4$ and $SnBr_4$

Element \ Molecule		$SiCl_4$	$SiBr_4$	$SnCl_4$	$SnBr_4$
Σ_1	..	0·001445	0·001579	0·001816	0·001976
Σ_2	..	0·02754	0·03249	0·05546	0·06645
Σ_3	..	0·00243	0·00318	0·00252	0·003286
Σ_{34}	..	−0·004265	−0·003125	0·00171	0·002501
Σ_4	..	0·02679	0·02812	0·03306	0·03558

TABLE V

Mean square amplitude quantities in Å² for $SiCl_4$, $SiBr_4$, $SnCl_4$ and $SnBr_4$ at 298° K.

Symbol \ Molecule		$SiCl_4$	$SiBr_4$	$SnCl_4$	SnB_4
σ_r	..	0·002184	0·002780	0·002344	0·002959
σ_{rr}	..	−0·00246	−0·0004	−0·000176	−0·000328
σ_α	..	0·02257	0·02489	0·03502	0·03994
$\sigma_{\alpha\alpha}$	..	−0·00459	−0·00542	−0·00924	−0·011075
$\sigma_{\alpha\alpha'}$	..	−0·00421	−0·00323	0·00196	−0·00436
$\sigma_{r\alpha}$	..	−0·001508	−0·001105	0·000601	0·000884
$\sigma_{r\alpha'}$	..	0·001508	0·001105	−0·000601	−0·000884
σ_δ	..	0·007263	0·009386	0·015697	0·018488
$\sigma_{\delta\delta}$	..	−0·00057	−0·000754	−0·001869	−0·002374
$\sigma_{\delta\delta'}$	..	0·000783	−0·000061	−0·000949	−0·001087
$\sigma_{r\delta}$	..	0·000711	0·001305	0·002116	0·002656
$\sigma_{r\delta'}$	..	0·000468	−0·000016	−0·000634	−0·001045

TABLE VI

Mean square parallel (u^2), perpendicular (v^2, w^2), amplitudes ($Å^2$) and mean amplitudes ($Å$) of vibration for $SiCl_4$, $SiBr_4$, $SnCl_4$ and $SnBr_4$ at 298° K.

Molecule	Pair	u^2 ($Å^2$)	v^2 ($Å^2$)	w^2 ($Å^2$)–	Mean amplitude Å
$SiCl_4$	Si – Cl	0·002184	0·00732	0·00732	0·04673
	Cl ··· Cl	0·007263	0·005221	0·00869	0·08521
$SiBr_4$	Si – Br	0·00278	0·00798	0·00798	0·05272
	Br ··· Br	0·009386	0·006759	0·010357	0·09687
$SnCl_4$	Sn – Cl	0·002344	0·01082	0·01082	0·04841
	Cl ··· Cl	0·015697	0·01171	0·01694	0·01230
$SnBr_4$	Sn – Br	0·002959	0·01221	0·01221	0·05439
	Br ··· Br	0·018488	0·013797	0·020006	0·13590

The most important ones of the mean square amplitude quantities are σ_r and σ_d representing the mean square amplitudes of vibration for the bonded and non-bonded interatomic distances respectively.

These results will prove very useful in the interpretation of the electron diffraction studies of these molecules.

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