ON THE CALCULATION OF THE CHANGE IN THE MEAN SQUARE AMPLITUDE VALUES OF SOME XY_4 TETRAHEDRAL TYPE MOLECULES

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A method is developed to calculate the change in the mean square amplitude matrix ($\delta\Sigma$) from Cyvin's secular equation through an internal coordinate Green's function representation. This method is tried on some XY_4 tetrahedral type molecules. The Σ elements thus obtained are used to fix the force field for these molecules.

1. Introduction

One of the useful methods for determining an unambiguous set of force constants is the Green function method [1–3]. It is specially suitable for molecules having isotopic data. The method of determining the change in potential energy constants going from one isotope to another is the method of Green's function utilizing the internal coordinate representation [4]. In this paper an attempt is made to develop a method to calculate the change in mean vibrational amplitude quantities utilizing Cyvin's secular equation method and Green's function in internal coordinate representation.

2. Theoretical consideration

The well known Cyvin's secular equation [5] is written as

$$|G^{-1}\Sigma - \Delta_k E| = 0, \tag{1}$$

for the parent molecule, where G, Σ have the usual meaning and

$$\Delta_k = \frac{h}{8\pi^2 c v_k} \coth\left(\frac{h c v_k}{2KT}\right). \tag{2}$$

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For the perturbed molecule the secular equation for the mean vibrational amplitudes becomes

$$|(K+\delta K)(\Sigma+\delta\Sigma)-\Delta E| = 0, \tag{3}$$

where $K = G^{-1}$.

Here δK accounts for the change in mass and geometry and $\delta\Sigma$ accounts for the change in mean amplitudes in going from the parent to the perturbed system. Equation (3) can be rewritten as

$$|K_p(\Sigma+\delta\Sigma)-\Delta E| = 0, \tag{4}$$

where $K_p = (K+\delta K) = G_p^{-1}$.

Factorizing out $(\Delta E - K_p\Sigma)$, the following determinantal equation is obtained

$$|I-J_p(\Delta)K_p\delta\Sigma| = 0, \tag{5}$$

and

$$|J_p^{-1}(\Delta)| \neq 0, \tag{6}$$

where

$$J_p(\Delta) = (\Delta E - K_p\Sigma)^{-1} = (\Delta E - G_p^{-1}\Sigma). \tag{7}$$

In equation (7), Δ represents the perturbed molecule and $J_p(\Delta)$ is Green's function for a fictitious molecule having the geometry and mass of the perturbed molecule and mean-square amplitudes of the unperturbed molecule.

The quantity $\delta\Sigma$ in equation (5) will contain $n(n+1)/2$ quantities corresponding to n^{th} order equation. However, it is reasonable to assume that the contribution to the change in mean-square amplitudes arises mainly from the diagonal terms. On this basis, the expressions for mean amplitudes for bonded (σ_{x-y}) and non-bonded $(\sigma_{y...y})$ atoms of XY_4 (Td) molecules are given by

$$\sigma_{x-y}^2 = \tfrac{1}{4}\left[\Sigma_{11}+3\Sigma_{33}\right], \tag{8}$$

$$\sigma_{y...y}^2 = \tfrac{1}{3}\left[2\Sigma_{11}+\frac{d^2}{3}\Sigma_{22}+2\Sigma_{33}+\frac{d^2}{2}\Sigma_{44}\right]. \tag{9}$$

Σ_{11} and Σ_{22} are the values of a (1×1) and e (2×2) species of vibration for the tetrahedral molecules. For f_2 species Σ elements for the parent $(\Sigma_{33}$ and $\Sigma_{44})$ are calculated from electron diffraction data. Using these values of Σ_{33} and Σ_{44} in Eq. (5), the change in mean-square amplitude matrix $(\delta\Sigma)$ and hence the Σ elements of the perturbed molecules were calculated.

The molecular constants are fixed from the calculated Σ elements through the method developed by Ramaswamy et al. [6] and are given below.

The symmetrized mean-square amplitudes are given by

$$\Sigma = L\Delta L = L_0 A\Delta\tilde{A}\tilde{L}_0, \tag{10}$$

where

$$L_0 = V\tau^{1/2},\tag{11}$$

V and τ are the eigen-vector and eigen-values of G and

$$A = \begin{vmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{vmatrix}.\tag{12}$$

Expansion of Eq. (10) for the f_2 sepcies of vibration yields the equations

$$\Sigma_{33} = C_\theta^2[L_{33}^{02}\Delta_{33} + L_{34}^{02}\Delta_{44}] + S_\theta^2[L_{33}^{02}\Delta_{44} + L_{34}^{02}\Delta_{33}] + 2S_\theta C_\theta[L_{33}^0 L_{34}^0(\Delta_{44} - \Delta_{33})].\tag{13}$$

$$\Sigma_{44} = C_\theta^2[L_{43}^{02}\Delta_{33} + L_{44}^{02}\Delta_{44}] + S_\theta^2[L_{43}^{02}\Delta_{44} + L_{44}^{02}\Delta_{33}] + 2S_\theta C_\theta[L_{43}^0 L_{44}^0(\Delta_{44} - \Delta_{33})],\tag{14}$$

where L_{ij}^0 are the elements of the L_0 matrix, $C_\theta = \cos\theta$ and $S_\theta = \sin\theta$.

Substituting the calculated values of Σ for the perturbed molecule fixes the parameter θ. Molecular parameters like potential energy constants and rotational distortion constants were calculated using θ and are presented in Table III.

3. Results and discussion

As seen from the Table II the changes in mean vibrational amplitudes ($\delta\Sigma_{33}$) between the parent and the perturbed molecule calculated through the present method agree well with the values obtained from electron diffraction data. But a considerable difference is noticed between the calculated and observed values of $\delta\Sigma_{44}$. This difference is due to the assumption $\Sigma_{34} = 0$ in the expression for calculating the mean amplitudes of vibration of non-bonded atoms (Eq. (8)). Hence Σ_{44} is not used in the evaluation of the force field and only Σ_{33} of the perturbed molecule is utilized in fixing the force field.

TABLE I

The observed vibrational frequencies (in cm⁻¹), bond distance (in Å) and mean amplitudes of vibration (in Å) for some XY_4 type molecules

Molecule	Vibrational frequencies				Ref.	Bond distance d_{x-y}	Ref.	Mean amplitudes of vibration		Ref.
	ν_1	ν_2	ν_3	ν_4				σ_{x-y}	$\sigma_{y...y}$	
CH_4	2916.5	1534	3018.7	1306	[9]	1.106	[10]	0.0781	0.123	[10]
CD_4	2085	1092	2259	996	[11]			0.0684	0.106	
GeH_4	1990	833	2112	819	[7]	1.528	[7]	—	—	
CCl_4	461.9	220	789.1	319.5	[12]	1.766	[13]	0.0505	0.0696	[13]
$GeCl_4$	396	132	453	172	[13]	2.113	[13]	0.0474	0.0979	[13]
$SnCl_4$	366	101.5	409.9	127.5	[14]	2.33	[15]	0.0499	0.1086	[16]
SiF_4	800	268	1031.8	389.35	[17, 20]	1.55	[18]	0.039	0.071	[19]
GeF_4	738	205	821.6	271	[18, 20]	1.67	[18]	—	—	

TABLE II

The change in mean square amplitudes between the parent and perturbed molecule and mean square amplitudes of the perturbed molecule

Parent	Perturbed	$\delta\Sigma_{33}$ Observed	$\delta\Sigma_{33}$ Predicted	$\delta\Sigma_{44}$ Observed	$\delta\Sigma_{44}$ Predicted	Σ_{33} Observed	Σ_{33} Predicted	Σ_{44} Observed	Σ_{44} Predicted
CH_4	CD_4	−0.001393	−0.001454	0.000218	0.004949	0.004828	0.004767	0.013499	0.018228
CH_4	GeH_3^*	0.001825	−0.001845	0.002551	0.005574	0.008046	0.008066	0.015832	0.018855
CCl_4	$GeCl_4$	−0.000520	−0.000619	0.002925	0.004221	0.002451	0.002352	0.003935	0.005231
CCl_4	$SnCl_4$	−0.000264	−0.000772	0.001534	0.006132	0.002707	0.002199	0.002544	0.007142
SiF_4	GeF_4^*	−0.000153	0.000037	0.001387	0.002751	0.001532	0.001722	0.004654	0.006018

* Calculated from the reported mean amplitudes of vibration.

TABLE III

Calculated mean vibrational amplitudes (in Å), parameter θ, symmetrized force constants (in mdyn/Å)[a] and rotational distortion constants (in Hz)

Molecule	Mean vibrational amplitudes		Ref.	Parameter	Force constants (f_2 species)			Ref.	Rotational distortion constants		Ref.
	σ_{x-y}	$\sigma_{y...y}$			F_{33}	F_{34}	F_{44}		D_J	D_{JK}	
CD_4	0.0677	0.1102	[P.W]	75°49′	5.2473[b]	0.7054	0.5026	[P.W]	0.701×10^6	0.269×10^6	[P.W]
	0.0684	0.106	[10]	77°13′	5.2530	0.7715	0.5206	[*]	0.722×10^6	0.259×10^6	[*]
				—	5.1250	0.3511	0.4400	[8]	0.758×10^6	0.345×10^6	[8]
GeH_4	0.0903	0.1588	[P.W]	10°31′	2.6047	0.0319	0.1926	[P.W]	1.141×10^6	0.931×10^6	[P.W]
	0.0902	0.1551	[8]	9°35′	2.6034	0.0068	0.1924	[**]	1.150×10^6	0.909×10^6	[**]
					2.6034	0.0009	0.1922	[7]	1.018×10^6	0.567×10^6	[7]
$GeCl_4$	0.0466	0.1023	[P.W]	26°55′	2.9645	0.3472	0.1895	[P.W]	123.005	155.143	[P.W]
	0.0474	0.0979	[13]	28°56′	3.0264	0.4058	0.2002	[*]	121.820	161.022	[*]
				—	2.6737	0.1289	0.1712	[6]	129.3	139.4	[6]
$SnCl_4$	0.0459	0.1249	[P.W]	16°10′	2.5937	0.1441	0.1095	[P.W]	107.955	144.200	[P.W]
	0.0499	0.1086	[16]	23°42′	2.6756	0.3471	0.1406	[*]	101.161	159.963	[*]
				—	2.6548	0.2121	0.1161	[6]	105.8	149.5	[6]
GeF_4	0.0401	0.0892	[P.W]	41°50′	6.1530	0.7796	0.3459	[P.W]	1.003×10^3	1.681×10^3	[P.W]
	0.0383	0.0849	[8]	34°27′	5.8571	0.3286	0.2780	[**]	1.177×10^3	1.714×10^3	[**]
				—	5.5579	0.3296	0.2781	[6]	1.0586×10^3	1.542×10^3	[6]

[a] 1 mdyn/Å = 10^2 N/m.

[b] The number of significant figures is retained to secure internal consistency in calculations.

* Calculated from the observed mean amplitudes of vibration.

** Calculated from the reported mean amplitudes of vibration.

The calculated mean amplitudes of vibration corresponding to bonded (σ_{x-y}) and non-bonded ($\sigma_{y...y}$) atoms for CD_4 and GeH_4 using CH_4 as the parent molecule, $GeCl_4$ and $SnCl_4$ using CCl_4 as the parent and GeF_4 using SiF_4 as the parent are in good agreement with electron diffraction results.

The potential energy constants evaluated from the calculated mean amplitudes of vibration through the parametric representation method are in good agreement with the values calculated from the electron diffraction data. It also agrees with the earlier calculation of Cleveland et al. [7] and Ranganathan [8].

Rotational distortion constants D_J and D_{JK} calculated by the above method compared well with earlier works [6, 8].

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