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ON THE CALCULATION OF THE CHANGE IN THE MEAN-SQUARE AMPLITUDE VALUES OF SOME XY_3 PYRAMIDAL TYPE MOLECULES

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The method of calculating the change in the mean-square amplitude quantities of Cyvin's secular equation through the internal coordinate Green's function representation is applied to some XY_3-pyramidal type molecules. To check the accuracy of this method other molecular constants were evaluated using the calculated Σ values and the parametric representation method.

1. *Introduction*

In an earlier paper [1] a method for calculating the change in the mean-square amplitude matrix ($\delta\Sigma$) from Cyvin's secular equation through the internal coordinate Green's function representation was described and was applied to some XY_4 (T_d) type molecules. To check the validity of the method it is extended to some XY_3-pyramidal type molecules for which unique force fields are known.

2. *Theoretical consideration*

With the procedure given in Ref. [1] the following determinental equation is obtained:

$$|I-J_p(\Delta)K_p\delta\Sigma| = 0 \tag{1}$$

and

$$|J_p^{-1}(\Delta)| = 0 \tag{2}$$

where

$$J_p(\Delta) = (\Delta E-K_p\Sigma)^{-1} = (\Delta E-G_p^{-1}\Sigma) \tag{3}$$

$J_p(\Delta)$ is the Green function for a fictious molecule having the geometry and mass of the perturbed molecule and mean square amplitudes of the unperturbed molecule.

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TABLE I

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

Parent	Perturbed	$\delta\Sigma_{11}$		$\delta\Sigma_{22}$		Σ_{11}		Σ_{22}		Ref.
		from edd	predicted	from edd	predicted	from edd	predicted	from edd	predicted	
NF_3	AsF_3	−0.000526*	−0.000644	0.001234	0.000851	0.001875	0.001757	0.002040	0.001656	pw
AsF_3	NF_3	0.000526	0.000584	−0.001234	−0.001097	0.002401	0.002459	0.000806	0.000944	pw
PH_3	NH_3	−0.001896	−0.002302	0.007803	0.009628	0.005329	0.004923 0.005089	0.024037	0.025864 0.022375	pw [3]
NH_3	PH_3	0.001896	0.001712	−0.007803	−0.008211	0.007225	0.007041 0.007059	0.016234	0.015826 0.015768	pw [3]
NH_3	AsH_3	0.002663	0.002403	−0.008674	−0.008983	0.007992	0.007732 0.007760	0.015363	0.015054 0.015044	pw [3]
NH_3	SbH_3	0.003582	0.003535	−0.011690	−0.009231	0.008911	0.008864 0.009646	0.012347	0.014805 0.014092	pw [3]

* This number of significant figures is retained for consistency in the calculations. edd = electron diffraction data, pw = present work.

The quantity $\delta\Sigma$ in equation (1) contains $n(n+1)/2$ quantities corresponding to an n-th order equation. In the present case there are six unknown quantities in the Σ matrix (three in a_1 species and three in e species) which are to be calculated. However, it is reasonable to assume that the contribution to the change in mean square amplitudes arises mainly from the diagonal terms. The expressions for the bonded and non-bonded mean amplitudes for XY_3-pyramidal type molecules are given by the well known relations

$$\sigma^2_{x-y} = \tfrac{1}{3}\,[2\Sigma_{11}+\Sigma_{33}] \tag{4}$$

$$\sigma^2_{y\ldots y} = \tfrac{2}{3}\,A^2[2\Sigma_{11}+\Sigma_{33}]+\tfrac{1}{3}\,B^2[\Sigma_{22}+2\Sigma_{44}], \tag{5}$$

where

$$A = \frac{d(1-\cos\alpha)}{p}; \quad B = \frac{d^2\sin\alpha}{p}; \quad p = 2d\sin(\alpha/2);$$

Σ_{11} and Σ_{22} are the values of the a_1 (2×2) species of vibration and Σ_{33} and Σ_{44} correspond to the e (2×2) species of vibration. Knowing the values of σ_{x-y} and $\sigma_{y\ldots y}$ from electron diffraction data one can calculate the Σ elements of equations (4) and (5). Using these values in equation (1), the $\delta\Sigma$ values for the perturbed molecule can be calculated. With these Σ values, σ_{x-y} and $\sigma_{y\ldots y}$ for the perturbed system were calculated and compared with the experimental data. These are summarized in Table I.

3. *Spectral data*

The molecular parameters, vibrational frequencies and other experimental data like rotational distortion constants, electron diffraction data etc., are taken from Ramaswamy and Sridharan [2].

4. *Results and discussion*

As seen from Table I, the changes in mean vibrational amplitudes calculated by this method for the perturbed molecules compare well with the values obtained from the electron diffraction data.

The calculated mean amplitudes of vibration corresponding to bonded (σ_{x-y}) and non-bonded ($\sigma_{y\ldots y}$) atoms for NF_3, AsF_3, PH_3, AsH_3, NH_3 and SbH_3 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 comparable with the values reported by Ramaswamy et al. [2] using the parametric method utilizing the observed Coriolis coupling constant, mean amplitudes of vibration and rotational distortion constants. It also compares with the values reported by Ponomarev and Khovrin [4], Mirri [5], Duncan and Mills [6] and Parisean and Overend [7].

Rotational distortion constants D_j, D_{jk} and D_k and Coriolis coupling constants ξ_3 and ξ_4 calculated by the above method compare well with the earlier workers as well as with the observed values. It will give an additional check on the utility of this method.

TABLE II

Calculated mean vibrational amplitudes (in Å), parameter ϕ and symmetrised force constants (in mdyn/Å) for some XY_3 pyramidal type molecules

Molecule	Mean vib. amplitudes			Parameter ϕ_a	Force constants (a_1 species) mdyn/Å			Parameter ϕ_e	Force constants (e species) mdyn/Å			Ref.
	σ_{x-y}	$\sigma_{y\ldots y}$	Ref.		F_{11}	F_{12}	F_{22}		F_{33}	F_{34}	F_{44}	
NF_3	0.0496*	0.0606	pw	22.916°	6.3459	0.6693	1.2555	16.578°	3.3486	−0.3110	0.9084	pw
	0.0490	0.0592	[17]	19°19′	6.2042	0.6404	1.2800	20°	3.4780	−0.3675	0.8869	[2]
				—	6.29	0.6418	1.2449	—	3.22	−0.2025	0.9310	[5]
				—	5.72	0.5908	1.5002	—	3.52	−0.3136	0.9257	[4]
AsF_3	0.0419	0.0641	pw	8.649°	4.3529	−0.4796	0.6386	18.202°	4.4110	−0.1779	0.3457	pw
	0.0433	0.0689	[18]	7° 48′	4.2421	−0.5465	0.6569	16° 43′	4.3644	−0.1454	0.3240	[2]
				—	4.80	−0.2808	0.5684	—	4.34	−0.1346	0.3143	[5]
				—	5.08	0.2448	0.4965	—	4.35	−0.1053	0.3184	[4]
NH_3	0.0702	0.1256	pw	73.662°	7.0574	−0.1420	0.4458	69.010°	6.3982	0.7073	0.7892	pw
	0.0730	0.1250	[19]	78° 30′	7.1209	0.3066	0.4539	83° 32′	6.9818	0.0236	0.6656	[2]
				—	7.075	0.780	0.532	—	7.038	−0.174	0.665	[6]
				—	6.981	1.215	0.666	—	6.963	0	0.666	[7]
PH_3	0.0839	0.1498	pw	33.267°	3.4638	0.1795	0.3387	45.410°	3.2690	0.0611	0.3790	pw
	0.0850	0.1517	[20]	40° 3′	3.4422	0.3024	0.3538	51° 19′	3.2840	−0.0517	0.3765	[2]
				—	3.402	0.200	0.340	—	3.466	−0.040	0.376	[6]
				—	3.306	0.530	0.393	—	3.270	−0.010	0.393	[7]
AsH_3	0.0879	0.1579	pw	10.498°	2.8560	0.1402	0.2897	9.583°	2.8780	−0.2592	0.3101	pw
	0.0894	0.1598	[20]	25° 44′	2.6246	0.5366	0.4174	6° 9′	2.8953	−0.0740	0.3001	[2]
				—	2.778	−0.250	0.312	—	2.892	−0.100	0.301	[6]
				—	2.785	0.322	0.309	—	2.896	0.131	0.309	[7]
SbH_3	0.0942	0.1739	pw	11.065°	2.2844	0.2186	0.2364	10.236°	2.2520	−0.2164	0.2336	pw
	0.0944	0.1636	[20]	18° 15′	2.1797	0.3988	0.2748	16°	2.2991	−0.0132	0.2085	[2]
				—	2.267	−0.200	0.215	—	2.297	−0.020	0.208	[6]
				—	2.206	0.258	0.214	—	2.239	0	0.214	[7]

* This number of significant figures is retained for consistency in the calculations. pw = present work.

TABLE III

Calculated and observed rotational distortion constants* and Coriolis coupling constant for some XY_3 pyramidal type molecule

Molecule	D_j	$-D_{jk}$	D_k	Ref.	ξ_3	ξ_4	$\xi_3+\xi_4$	Ref.
NF_3	14.39	22.59	10.07	pw	0.8201	−0.9062	−0.0861	pw
	14.53	22.69	—	[5]	0.81	−0.90	−0.1	[4]
AsF_3	4.50	4.49	2.10	pw	0.1322	−0.4268	−0.2946	pw
	4.63	6.17	—	[5]	0.21	−0.44	−0.23	[4]
NH_3	20.24	34.20	21.61	pw	0.4578	−0.6715	−0.2137	pw
	24.27	43.65	23.5	[8]	0.06	−0.26	−0.20	[6]
PH_3	3.80	5.25	3.98	pw	0.0955	−0.5272	−0.4317	pw
	3.95	5.20	4.09	[9]	0.02	−0.43	−0.41	[6]
AsH_3	2.58	2.61	2.20	pw	−0.1398	−0.3291	−0.4689	pw
	2.13	—	—	[10]	−0.06	−0.43	−0.49	[6]
SbH_3	2.88	3.06	2.43	pw	−0.2392	−0.2348	−0.4747	pw
	—	—	—	—	0.01	−0.43	−0.42	[6]

* Rotational distortion constants for fluorides are in KHz and for hydrides in MHz.

TABLE IV

Calculated and observed frequencies for some XY_3 pyramidal type molecules

Molecule	Vibrational frequencies (cm^{-1})				Ref.
	ν_1	ν_2	ν_3	ν_4	
$^{15}NF_3$	1015.3	623	894.6	471.1	pw
	1009	643	886	492	[11–13]
ND_3	2520.8	772.4	2669.5	1211.6	pw
	2495	793	2652	1225	[8, 14]
PD_3	1749.3	763.9	1719.8	821.6	pw
	1760	759	1720	822	[6]
AsD_3	1569.5	697.7	1583.6	718.9	pw
	1571	696	1582	719	[15]
SbD_3	1409.5	568.8	1400.9	599.4	pw
	1409	569	1404	600	[16]

The calculated vibrational frequencies for the isotopically substituted molecules are summarized in Table IV along with the observed values which are in very good agreement.

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