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Vibrational analysis of the isotopic methylammonium ions

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Abstract. A complete vibrational analysis of the methyl ammonium ion $CH_3NH_3^+$, and of $CD_3NH_3^+$, $CH_3ND_3^+$ and $CD_3ND_3^+$ is described in this paper. A General valence Force Field has been computed for these ions, belonging to C_{3v} sysmmetry, using the fundamental frequencies obtained from the infrared spectra. The mean square amplitudes and shrinkage constants and Coriolis coupling constants have also been calculated for the first time and presented here.

Keywords. Symmetry; vibrational frequencies; normal co-ordinate analysis; molecular constants.

1. Introduction

The four isotopic methylammonium ions possess C_{3v} symmetry. Their fundamental vibrations can be classified according to the irreducible representations (species) of the point group C_{3v} :

$$\Gamma = 5a_1 + a_2 + 6e.$$

The torsional mode a_2 is infrared inactive under C_{3v} symmetry. Assignments of the infrared-active fundamentals have been made for each of these ions by Oxton *et al* (1977). These assignments were based on the previous infrared studies Waldron (1953), Cabana and Sandorfy (1962) and Theoret and Sandorfy (1967), of the ion with simple halides. The structural parameters, vibrational frequencies and the orthonormal set of symmetry co-ordinates used in the present calculations have been taken from the investigation of Oxton *et al* (1977). The set of internal co-ordinates chosen, numbering of atoms and the orientation of Cartesian co-ordinates axes of methylammonium ion are shown in figure 1. All the angles were assumed to be tetrahedral.

Normal coordinate analysis has been performed by Oxton *et al* (1977). However, for continuity, the General Valence Force Field (GVFF) has been repeated in the present investigation. The mean amplitudes of vibration, the generalised mean square amplitudes of vibration and shrinkage constant and Coriolis coupling coefficients have been computed for the first time and reported here.

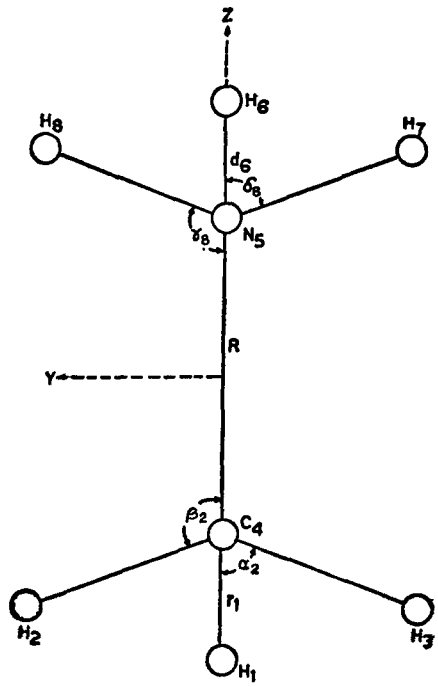

Figure 1. Internal co-ordinates, numbering of atoms and orientation of the principal axes in the isotopic methyl ammonium ions.

2. Theoretical considerations

2.1. *Molecular force field*

GVFF is used to obtain the force constants. A reliable set of force constants has been obtained by Wilson's (1939) F-G Matrix method.

2.2. *Mean-square amplitudes of vibration and shrinkage effect*

The symmetrised mean square amplitude matrix Σ has been evaluated using the relation (Cyvin 1960).

$$\Sigma = L \triangle L',$$

where L's are characteristic vectors and $\triangle$ is a diagonal matrix consisting of the mean square values of the normal co-ordinates given by (Block 1932). The generalised mean square amplitudes (Morino and Hirota 1955) $\langle(\triangle z)^2\rangle$, $\langle(\triangle y)^2\rangle$ and $\langle(\triangle x)^2\rangle$ and the mean cross products $\langle(\triangle x)\ (\triangle y)\rangle$, $\langle(\triangle y)\ (\triangle z)\rangle$ and $\langle(\triangle z)\ (\triangle x)\rangle$ have been evaluated using the Σ matrix from the relation,

$$X = A\ S \text{ where}$$

$$A = M^{-1}\ B'\ G^{-1}.$$

Table 1. Internal force constants of methylammonium ion (m. dyne/Å).

f_R	4·6386	$f_{r\gamma}$	0·0416
f_r	4·7696	$f_{r\delta}$	−0·0001
f_d	5·7320	$f_{d\alpha}$	0·0122
f_{rr}	0·0466	$f_{d\beta}$	0·0198
f_{dd}	0·0890	$f_{d\gamma}$	0·0697
$f_\alpha - f_{\alpha\alpha}$	0·3581	$f_{d\delta}$	0·0529
$f_\beta - f_{\beta\beta}$	0·4340	$f_{\alpha\beta}$	−0·0918
$f_\gamma - f_{\gamma\gamma}$	0·6521	$f_{\alpha\gamma}$	0·0467
$f_\delta - f_{\delta\delta}$	0·5373	$f_{\alpha\delta}$	0·0020
f_{Rr}	0·1002	$f_{\beta\gamma}$	−0·1016
f_{Rd}	0·0947	$f_{\beta\delta}$	0·0217
f_{rd}	−0·0076	$f_{\gamma\delta}$	0·0287
$f_{r\alpha}$	0·0247	$(1{\cdot}258 f_{R\alpha} - 1{\cdot}191 f_{R\beta}) =$	−0·4229
$f_{r\beta}$	0·0366	$(1{\cdot}258 f_{R\delta} - 1{\cdot}191 f_{R\gamma}) =$	−0·3160

Table 2. Mean square amplitudes of vibration of the isotopic methylammonium ions at 300° K in 10^{-4} Å^2.

	$CH_3NH_3^+$	$CH_3ND_3^+$	$CD_3NH_3^+$	$CD_3ND_3^+$
σ_R	25·35	25·16	25·37	25·22
σ_r	61·46	61·46	44·87	44·64
σ_d	55·80	40·46	55·74	40·40
σ_{rr}	−1·13	−1·13	−1·41	−1·29
σ_{dd}	−1·10	−0·81	−1·11	−0·90
$\sigma_\alpha - \sigma_{\alpha\alpha}$	362·40	413·00	262·20	280·60
$\sigma_\beta - \sigma_{\beta\beta}$	267·90	310·50	196·50	222·80
$\sigma_\gamma - \sigma_{\gamma\gamma}$	208·20	134.80	228·40	157·90
$\sigma_\delta - \sigma_{\delta\delta}$	287·40	206·90	289.00	208·40
σ_{Rr}	−1·55	−1·55	−2·14	−2·14
σ_{Rd}	−1·20	−1·71	−1·20	−1·70
σ_{rd}	0	0	0	0
$\sigma_{r\alpha}$	−7·15	−7·15	−10·75	−10·67
$\sigma_{r\beta}$	−8·14	−8·14	−10·93	−10·85
$\sigma_{r\gamma}$	−5·77	−5·77	−7·75	−7·70
$\sigma_{r\delta}$	0	0	0	0
$\sigma_{d\alpha}$	0	0	0	0
$\sigma_{\alpha\beta}$	−4·39	−5·86	−4·39	−5·87
$\sigma_{d\gamma}$	−6·53	−8·71	−6·52	−8·71
$\sigma_{\alpha\delta}$	−5·43	−8·29	−5·43	−8·30
$\sigma_{\alpha\beta}$	16·33	62·03	18·35	40·48
$\sigma_{\alpha\gamma}$	−28·94	−38·68	−33·00	−39·00
$\sigma_{\alpha\delta}$	0	0	0	0
$\sigma_{\beta\gamma}$	42·66	50·20	51·51	57·63
$\sigma_{\beta\delta}$	−12·26	−15·94	−12·33	−16·03
$\sigma_{\gamma\delta}$	−27·16	−17·68	−21·74	−13·07
$[1{\cdot}258\sigma_{R\alpha} - 1{\cdot}191\sigma_{R\beta}]$	27·21	29·10	27·70	28·29
$[1{\cdot}258\sigma_{R\delta} - 1{\cdot}191\sigma_{R\gamma}]$	20·25	20·89	20·48	21·01

Table 3. Generalised mean square amplitudes of vibration in 10^{-4} Å^2 and shrinkage constants in Å of the isotopic methylammonium ions.

Ion	Atom pair	Parallel	Perpendicular		Mean cross products			Shrinkages
		$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$	$\langle(\Delta x)(\Delta y)\rangle$	$\langle(\Delta y)(\Delta z)\rangle$	$\langle(\Delta z)(\Delta x)\rangle$	
$CH_3NH_3^+$	C—N	26·74	8·71	8·71	0	0	0	—
	C—H_1	61·43	145·00	114·90	0	0	− 2·12	—
	N—H_6	55·01	101·11	82·79	0	0	34·20	—
	H_1...H_2	165·79	266·92	99·73	−9·21	3·69	0·16	0·0081
	H_6...H_8	144·73	218·75	84·79	9·45	0	0·02	0·0061
	C...H_6	104·54	82·07	69·09	0	0	−37·35	0·0021
	N...H_1	115·00	85·31	35·41	0	0	41·34	0·0004
	N_1...H_6	250·97	125·87	146·66	0	0	− 2·66	−0·0417
$CH_3ND_3^+$	C—N	25·15	11·81	11·81	0	0	0	—
	C—H_1	61·41	159·02	139·99	0	0	− 2·22	—
	N—D_6	40·45	66·16	57·65	0	0	26·24	—
	H_1...H_2	180·38	304·23	114·08	−8·31	−0·01	0·01	0·0039
	D_6...D_8	101·17	120·02	58·67	3·49	0·01	0·01	0·0064
	C...D_6	71·57	51·19	46·20	0	0	−19·25	0·0093
	N...H_1	123·27	91·57	103·20	0	0	50·02	−0·0038
	H_1...D_6	271·73	91·76	145·25	0	0	45·87	−0·0560
$CD_3NH_3^+$	C—N	25·34	13·24	13·24	0	0	0	—
	C—D_1	44·79	96·45	71·27	0	0	−2·61	—
	N—H_6	55·70	104·24	85·51	0	0	35·41	—
	D_1...D_2	117·20	166·52	71·48	−2·64	−0·01	0·01	0·0065
	H_6...H_8	145·19	243·12	85·21	9·97	0	0·03	0·0052
	C...H_6	101·67	88·76	75·53	0	0	−45·83	0·0022
	N...D_1	83·90	48·85	51·18	0	0	25·27	0·0050
	D_1...H_6	209·51	90·23	112·75	0	0	−11·60	−0·0372
$CD_3ND_3^+$	C—N	25·26	16·78	16·78	0	0	0	—
	C—D_1	45·23	104·32	92·56	0	0	− 2·94	—
	N—D_6	40·37	69·31	60·02	0	0	26·15	—
	D_1...D_2	117·86	186·30	72·33	−1·83	−0·04	0·01	0·0095
	D_6...D_8	101·62	143·77	59·37	4·06	−0·02	− 0·05	0·0075
	C...D_6	77·62	60·29	51·14	0	0	−26·36	0·0068
	N...D_1	89·32	65·92	57·93	0	0	37·18	0·0032
	D_1...D_6	173·98	72·86	90·92	0	0	− 0·54	−0·0295

2.3. *Coriolis coupling coefficients*

The active couplings for these ions are $a_1 \times e$ and $e \times e$, belonging to ξ^x and ξ^z respectively. The Coriolis coupling coefficients have been calculated from the relation given by Meal and Polo (1956)

$$\xi^a = L^{-1} C^a (L^{-1})',$$

where C^a matrix is obtained from the geometry and atomic masses.

3. Results and discussion

The internal force constants for the methylammonium ion using GVFF are presented in table 1. These values compare very well with those calculated by Oxton *et al* (1977). In general, the important stretching and bending force constants are found to be the same for all the four isotopic ions, as expected.

The mean-square amplitude quantities (σ), calculated at 300° K are listed in table 2. The generalised mean-square amplitudes of vibration and the shrinkage constants are given in table 3. The parallel mean-square amplitudes $\langle(\triangle z)^2\rangle$ compare very well with the mean-square amplitude quantities (σ). Also for C—H and N—H bonds, the perpendicular mean square amplitudes of vibration are found to be greater than the parallel mean-square amplitudes.

The significant Coriolis coupling coefficients for $a_1 \times e$ and $e \times e$ couplings are reported in table 4. The following rules are found to be satisfied for the various couplings:

$a \times e$ coupling

$$\zeta^x_{a_1 \times e_a} = \zeta^y_{a_1 \times e_b} = 0$$

$$\zeta^x_{a_1 \times e_b} = -\zeta^y_{a_1 \times e_a}$$

$e \times e$ coupling

$$\sum_{i=7}^{12} \zeta^z_{il} = I_A/2I_B$$

where I_A and I_B are the principal moments of inertia.

The Coriolis coupling coefficients facilitate the analysis of vibration-rotation spectra.

4. Conclusions

It is expected that the analysis presented here would help us in knowing the spectroscopic properties of the ion in an environment of lower symmetry, which is

Table 4. Coriolis coupling coefficients of the isotopic methylammonium ions.

	$CH_3NH^+_3$	$CH_3ND_3^+$	$CD_3NH_3^+$	$CD_3ND_3^+$
	Coupling $a_1 \times e$			
$\zeta^x_{1,11}$	− 0·6385	− 0·6263	− 0·6256	− 0·6299
$\zeta^x_{2,12}$	0·6054	0·5173	0·6105	0·5229
$\zeta^x_{4,7}$	− 0·7350	0·7213	0·7269	− 0·7152
$\zeta^x_{5,8}$	0·7330	0·6920	0·7308	0·6890
$\zeta^x_{5,10}$	0·5536	0·4840	0·5549	0·4941
	Coupling $e \times e$			
$\zeta^z_{7,7}$	0·1015	0·1015	0·1844	0·1844
$\zeta^z_{7,9}$	0·6448	0·6172	0·6220	0·6225
$\zeta^z_{7,11}$	− 0·6877	− 0·7144	− 0·6975	−0·6946
$\zeta^z_{8,8}$	0·0883	0·1624	0·0883	0·1624
$\zeta^z_{8,10}$	0·8030	0·8345	0·8079	0·8450
$\zeta^z_{8,12}$	− 0·4971	− 0·4262	− 0·4898	− 0·4064
$\zeta^z_{9,9}$	− 0·3294	− 0·3178	− 0·3259	− 0·3307
$\zeta^z_{10,10}$	− 0·3267	− 0·3541	− 0·3265	− 0·3511
$\zeta^z_{11,11}$	0·2907	0·2807	0·2519	0·2494
$\zeta^z_{12,12}$	0·2962	0·2906	0·2808	0·2633

Other couplings are found to be insignificant.

a subject of recent interest. The mean square amplitudes of vibration, the generalised mean square amplitudes and shrinkage constants and Coriolis coupling constants have also been calculated for the first time and presented here. The mean amplitude calculations are useful in the interpretation of electron diffraction studies in the molecular structure determinations and the shrinkage constants are helpful in the refinement of bond lengths obtained experimentally. The Coriolis constants are used in the interpretation of vibrational spectra of molecules.

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