four C−hal stretching vibrations [4] in the present molecule.

We are indebted to K. Ruzicka for synthetic work and to O. H. Ellestad at the Chemical Laboratory V, H. C. Ørsted Institute, Copenhagen, for recording the far infrared spectra.

1. Klæboe, P., Lothe, J. J. and Lunde, K. Acta Chem. Scand. 11 (1957) 1677.
2. Klæboe, P. Acta Chem. Scand. 25 (1971) 695.
3. Horntvedt, H. T. and Klæboe, P. Acta Chem. Scand. 25 (1971) 772.
4. Altona, C., Hageman, H. J. and Havinga, E. Spectrochim. Acta A 24 (1968) 633.

Force Fields of the Methylammonium Halides in the α-Phases

G. BORCH

Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark

and

U. ANTHONI and P. H. NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

In a recent communication by Whalley [1] it was pointed out that the infrared spectra of the α-phases (stable at room temperature) of methylammonium chloride, bromide, and iodide cannot be interpreted except by taking into account the orientational disorder of the cations of C_{3v} symmetry in the tetragonal field produced by the halide ions. It was shown that the vibrations of species A_1 are almost independent of this disorder and appear as sligthly perturbed fundamentals in the infrared spectra. In contrast, the vibrations of species E couple to give several infrared-active combinations. Owing to overlap these appear as broad, Gaussian absorption bands. This difference in shape is clearly observed in the infrared spectra of the methylammonium halides and three deuterated compounds.[2,3]

A harmonic force field for organic ammonium compounds has not yet been described, but is needed as a basis for study of the vibrational spectra of hydrazinium compounds.[4] In the light of the foregoing discussion it follows that only the experimental frequencies of species A_1 of the methylammonium halides can be considered suitable for developing such a force field. The maxima of the bands of species E are produced by superposition of many sub-bands and should be considered only rough approximations to the frequencies of the fundamental vibrations of the isolated methylammonium ion. However, a comparison of the infrared spectra of the α- and the γ-phases of the four isotopic species of methylammonium chloride [3] shows that the main effect of orientational disorder on the absorption bands of species E is to broaden the bands without changing the position of the maxima. The fundamentals of species E have therefore been included in the experimental material used for determination of the force fields.

The geometry of methylammonium chloride [5] and bromide [6] is partly known, but comparable data do not exist for the iodide. Therefore, all calculations have been carried out assuming tetrahedral bond angles and identical bond lengths: $C−H = 1.093$ Å, $N−H = 1.011$ Å, and $C−N = 1.465$ Å. The methylammonium ion was described in terms of C_{3v} symmetry, i.e. with the irreducible representation $5A_1 + A_2 + 6E$. The torsional vibration of species A_2 was omitted in the normal coordinate analyses. The fundamental frequencies (Table 2) were taken from the paper by Theoret and Sandorfy.[3]

The symmetry coordinates were constructed from the internal coordinates (Table 1) in the usual way. The two angle deformation redundants of species A_1 were removed automatically during the calculations. The final force constants for the three methylammonium halides are listed in Table 1. Most of the force constants change regularly from the chloride to the iodide. The decreasing strength in the $N^+ − H \cdots X^-$ hydrogen bond in the sequence $X = Cl$, Br, I is reflected in increasing values of K_r' and decreasing values of $H_{\alpha'}, H_{\beta'}$, and K_R.

Table 1. Molecular parameters for methylammonium chloride, bromide, and iodide.

Atoms involved	Internal coordinates	Force constants [a]	Value of force constants [b] for		
			chloride	bromide	iodide
CH/CD	r	K_r F_r	4.747 0.077	4.743 0.078	4.757 0.092
NH/ND	r′	K_r' F_r'	5.16 0.06	5.16 0.06	5.25 0.09
C−N	R	K_R	4.82	4.77	4.72
HCH/DCD	α	H_α	0.536	0.526	0.522
HCN/DCN	β	H_β F_β	0.797 −0.023	0.788 −0.021	0.781 −0.019
HNH/DND	α′	H_α'	0.546	0.542	0.540
HNC/DNC	β′	H_β' F_β'	0.719 −0.001	0.672 −0.003	0.648 −0.006
CN/HCN	R,β	$F_{R\beta}$	0.404	0.422	0.445
CN/HNC	R,β′	$F_{R\beta}'$	0.312	0.303	0.294
HCN/HNC	β,β′	$f_{\beta\beta}'^t$ $f_{\beta\beta}'^g$	0.087 −0.003	0.089 −0.007	0.090 −0.010

[a] The nomenclature of Ref. 7 has been used.
[b] In units of mdyne/Å (stretching constants), mdyne/Å(rad)^2 (bending constants) and mdyne/rad (stretch/bend interaction constants).

Table 2. Calculated and observed frequencies (cm^{-1}) and potential energy distributions for methylammonium chloride, bromide, and iodide in the α-phases.

	Species	Cl		Br		I		Description [b]
		Calc.	Obs. [a]	Calc.	Obs. [a]	Calc.	Obs. [a]	
CH$_3$NH$_3$	A$_1$	3021	2993	3021	3035	3064	3012	νNH(100)
		2917	2917	2917	2926	2929	2924	νCH(100)
		1535	1534	1503	1500	1482	1486	δNH$_3$(100)
		1430	1427	1417	1408	1409	1406	δCH$_3$(100)
		1008	1004	1001	995	992	991	νCN(100)
	E	3075	3080	3075	3085	3093	3098	νNH(100)
		2966	2963	2965	2967	2964	2963	νCH(100)
		1590	1578	1580	1572	1575	1564	δNH$_3$(90−92)
		1472	1463	1459	1449	1454	1451	δCH$_3$(83−84), ϱCH$_3$(16−17)
		1269	1265	1253	1255	1246	1248	ϱNH$_3$(40−43), ϱCH$_3$(37−43), δCH$_3$(13−14)
		955	954	931	921	917	912	ϱCH$_3$(42−45), ϱNH$_3$(47−51)

Table 2. Continued.

CH$_3$ND$_3$	A$_1$	2171	2197	2170	2213^c	2200	2311	νND(100)
		2917	—	2917	2921	2929	2926	νCH(100)
		1180	1178	1159	1157	1145	1152	δND$_3$(72−77), νCN(23−28)
		1430	1427	1417	1410	1409	1406	δCH$_3$(100)
		955	954	946	945^d	936	940^c	νCN(86−90), δND$_3$(10−14)
	E	2282	2275	2281	2316^c	2294	2379	νND(100)
		2966	2970	2965	2954	2964	2954	νCH(100)
		1138	1150	1132	1140	1129	1140	δND$_3$(95)
		1470	1462	1457	1448	1451	1445	δCH$_3$(85−86), ϱCH$_3$(14−15)
		776	775	751	747	739	738	ϱND$_3$(76−77), ϱCH$_3$(19−20)
		1184	1188	1175	1140	1170	1175	ϱCH$_3$(71−72), δCH$_3$(13−14), ϱND$_3$(14−16)
CD$_3$NH$_3$	A$_1$	3021	2990	3021	2980^c	3064	3040^c	νNH(100)
		2102	2100	2101	2086^c	2109	—	νCD(100)
		1535	1534	1503	1494	1482	1480	δNH$_3$(100)
		1111	1115	1093	1099^c	1077	1093^c	δCD$_3$(69−70), νCN(30−31)
		942	945	942	945	943	937	νCN(81−88), δCD$_3$(12−19)
	E	3075	3080	3075	3020	3093	3070	νNH(100)
		2219	2220^c	2217	2225	2216	2226^c	νCD(100)
		1589	1578	1579	1576	1574	1564	δNH$_3$(90−92)
		1051	1062	1041	1050	1037	1040	δCD$_3$(92−94)
		1185	1177	1161	1157	1150	1147	ϱNH$_3$(73−76), ϱCD$_3$(15−20)
		783	790	770	770	761	760	ϱCD$_3$(70−73), ϱNH$_3$(20−25)
CD$_3$ND$_3$	A$_1$	2171	2180	2171	2152	2201	2311^c	νND(100)
		2101	2095^c	2101	2090^c	2109	2129^c	νCD(100)
		1180	1184	1158	1160	1144	1157	δND$_3$(73−76), νCN(24−26)
		1102	1105^c	1087	1084	1074	1082	δCD$_3$(78−83), νCN(16−17)
		897	900	893	900^c	890	891	νCN(78−80), δCD$_3$(7−13), δND$_3$(8−13)
	E	2283	2285	2282	2280^c	2295	2379	νND(97−98)
		2216	2239^c	2214	2213^c	2214	2181^c	νCD(96−99)
		1139	1150	1133	1140	1130	1148^c	δND$_3$(95−97)
		1050	1058	1041	1050^c	1037	1038	δCD$_3$(89−90), ϱCD$_3$(10−11)
		1010	1015	997	1005	991	1005	ϱND$_3$(43−46), ϱCD$_3$(44−48)
		689	692	672	664	662	658	ϱCD$_3$(43−45), ϱND$_3$(48−53)

^{a} The observed values are given in Ref. 3.

^{b} The following abbreviations have been used: ν=stretching, δ=deformation, ϱ=rocking. The rounded percentage potential energy distribution values are shown in parenthesis; contributions under 10 % have been neglected. The intervals stated show the variation from chloride to iodide.

^{c} β-phase.

^{d} γ-phase.

The calculated frequencies and a description of the fundamentals based on the potential energy distribution are given in Table 2. The calculations showed that the potential energy distributions were almost identical for all three halides, and the results, apart from minor coupling effects, support the assignments of Theoret and Sandorfy.[3]

1. Whalley, E. *J. Chem. Phys.* **51** (1969) 4040.
2. Cabana, A. and Sandorfy, C. *Spectrochim. Acta* **18** (1962) 843.
3. Theoret, A. and Sandorfy, C. *Spectrochim. Acta* **23** (1967) 519.
4. Anthoni, U., Dahl, B. M., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **24** (1970) 959.
5. Hughes, E. W. and Lipscomb, W. N. *J. Am. Chem. Soc.* **68** (1946) 1970.
6. Gabe, E. J. *Acta Cryst.* **14** (1961) 1296.
7. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta* **21** (1965) 169.