RAMAN SPECTRUM OF METHYLAMMONIUM CHLORIDE (CH_3NH_3Cl) IN THE SOLID STATE AND IN SOLUTION

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ABSTRACT

Several workers have investigated the infrared spectrum of methylammonium chloride and yet its Raman spectrum in the solid state was hitherto unknown. As some alums containing this $CH_3N^+H_3$ *are known to be ferroelectric and as the Raman spectrum of* α-MAC *can elulcidate the symmetry and magnitude of the crystal field effects on the vibrations of the* $CH_3N^+H_3$ *ion, we are reporting here the new Raman data on* $\alpha-$MAC. *The Raman shifts observed in the room temperature crystalline phase are 54, 87, 184, 960, 1000, 1240, 1439, 1465, 2783, 2826, 2904, 2963, and 3020* cm^{-1}. *An analysis of the spectrum leads us to conclude that the correlation coupling effect on the* $CH_3N^+H_3$ *ion is small. No line is observed in the indicator band region. The presence of intense Raman lines in the high frequency region have been attributed to a Fermi resonance between the* C-H-*stretching frequency and the harmonic of* C-H *bending vibrations.*

INTRODUCTION

The Raman spectrum of methylammonium chloride ($CH_3N^+H_3\,Cl^-$) in H_2O (44% solution) and in D_2O (36% solution) was investigated by Edsall J. T.[1] and by Edsall J. T. and Scheinberg, H.[2] as part of their investigations on the Raman spectra of amino-acids and related groups. The Raman spectrum of $MeNH_3Cl$ solution in NH_3 at room temperature was observed and compared with that in aqueous solution by Koyo Aida[3]. On the other hand the infrared spectrum of methyl ammonium chloride has been investigated in the solid phase by Waldron, R. D.[4] and by Cabanna, A and Sandorfy, C[5] and several amine hydrohalides by other workers also [6,7,8,9,10]. Among them Waldron used polarized infrared to analyse the absorption maxima in terms of the known crystal structure of α-methyl ammonium chloride (hereafter referred to as

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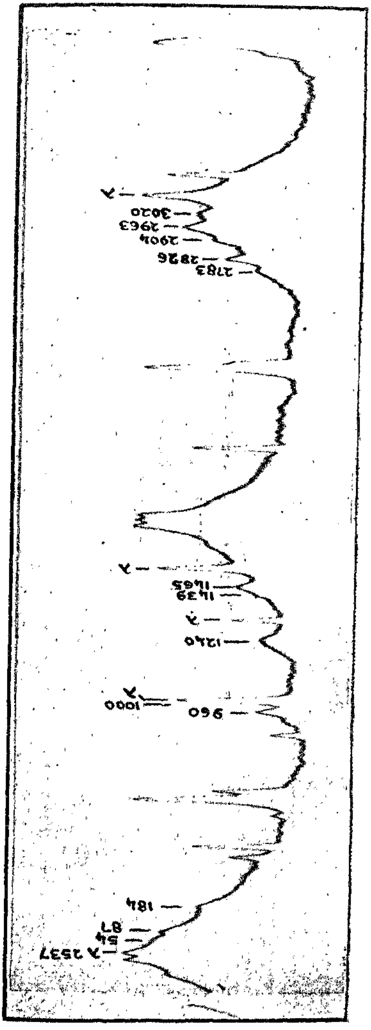

PLATE I (*a*)

Raman Spectrum of Crystalline power of $\alpha - \mathrm{CH}_2{}^+\mathrm{NH}_3\,\mathrm{Cl}$

PLATE I (*b*)

Raman Spectrum of the aqueous solution of CH_3+NH_3Cl

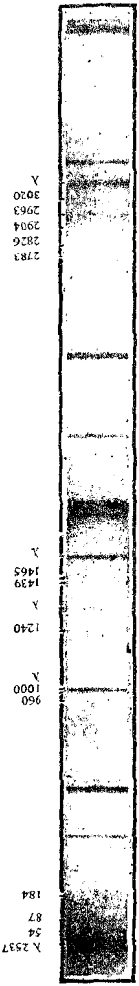

PLATE II (*a*)

Microphotometer record of the Raman spectrum of Crystalline α—MAC

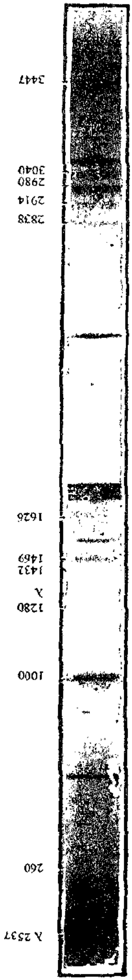

PLATE II (*b*)

Microphotometer record of the Raman spectrum of aqueous solution of MAC

α-*MAC*). Also by making use of the fact that the methylammonium ion is isoelectronic with the ethane molecule and hence the vibration spectra of the two will be similar, Waldron arrived at the conclusion that at room temferature the distortion of the methylammonium ion by the crystalline environment is so slight as to be undetectable. Since a study of the Raman spectrum of $\alpha-MAC$ in the crystalline state will throw light on the site symmetry of the CH_3NH_3 groups and the unique system of hydrogen bonds that this crystal exhibits, the present study was undertaken. To enable a reliable assignment of the hydrogen bonded vibrations and also to clarify the nature and origin of the bands in the region of 2050 cm^{-1} the Raman spectrum of the aqueous solution was also reinvestigated.

2. EXPERIMENTAL DETAILS

Methylammonium chloride, a product of E. Merck and of reagent quality was dehydrated under vacuum and since crystallization from an alcoholic solution did not give crystals big enough for single crystal work, the small crystals of the compound were put into a fused silica test tube and closed. The crystals were illuminated through the cylindrical wall of the container and the scattered light was gathered along the axis of the tube. For the study of the solution, a 43% aqueous solution of $CH_3N^+H_3\,Cl^-$ was acidified with hydrochloric acid (final concentration ~ 2% solution of *HCl*) to prevent hydrolysis and after short heating (~ 75°C), the solution was shaken with charcoal and filtered into the silica Raman tube.

λ2537 radiation from a watercooled and magnet controlled quartz arc was used for exciting the Raman spectra and they were recorded with a Hilger medium quartz spectrograph. In the case of the solution, the polarization of the Raman lines was studied by standard methods using a Wollaston prism. With a slit width of 0.035 mm. exposures of the order of 25 hours were necessary for the solid and for the water solution and about 60 hours for the polarization pictures. Ilford Zenith Astronomical plates were employed for recording the spectra.

3. RESULTS AND DISCUSSION

The Raman spectra of the crystalline powder and the aqueous solution are given in Figs. 1 (*a*) and 1 (*b*) while the corresponding microphotometer records have been given in Figs. 2 (*a*) and 2 (*b*). The observed frequency shifts of the Raman lines in the solid phase and in solution, the polarization characteristic of the Raman lines in the case of the solution are given in Table I. The infrared spectrum of $\alpha-MAC$ was recorded by subliming the substance under vacuum directly on to a *KBr* plate and with the help of a Carl Zeiss *UR* 10 spectrometer. The observed absorption maxima agreed well with those reported earlier by Waldron and have also been included in the same table.

Methylammonium chloride (CH_3NH_3Cl) crystallizes in the tetragonal system with the space group D^7_{4h} ($P\ 4/n\ mm$) at room temperature and with the cell dimensions $a_0 = 6.04$ Å and $c = 5.05$ Å. There are two molecules per unit cell according to Hughes, E. W. and Lipscomb, W. N.[11]. They also showed that the non-centrosymmetric structure proposed earlier by Hendricks, S. B.[12] is wrong. A striking feature of the structure of the room temperature α-phase of *MAC* is that the *C* and *N* are located on the fourfold axis of symmetry and since the free ion symmetry of the methyl-ammonium ion is C_{3v}, it is believed that in order that the hydrogens of the $CH_3N^+H_3$ groups can conform to the observed space group of the crystal, they randomize their orientation either by disordering or by rotation around the *C-N* axis. Also it was found that the formal charge on the N^+H_3 group does not shorten the *C-N* bond appreciably below the normal covalent value of 1.47 Å. *MAC* is known to undergo two transitions at lower temperatures, one at −55°C and the other at −190°C and the structures of the γ and β phase have yet to be determined.

Methylammonium ion, which is isoelectronic with ethane molecule has under C_{3v} symmetry, 5 totally symmetric (A_1) type vibrations and 6 doubly degenerate (E) type vibrations, all of them being allowed both in Raman effect and infrared absorption and one torsional mode of type (A_2) which is inactive in both. If we assume that the crystalline field and correlation coupling effects are small, then the A_1 type vibrations will be having their transition moments along the fourfold axis in absorption and will give polarized Raman lines while the E type vibrations will show perpendicular polarization in infrared absorption and lead to depolarized Raman lines. If however the three fold axis of symmetry of the methylammonium ion is removed in the crystal because of the perturbation by the neighbouring ions in the crystal, the degeneracies will be removed and the A_2 vibration will also become active. An analysis of the observed Raman lines in the light of these theoretical expectations shows that in the α-phase, there is only a broadening of the E-type rocking and bending vibrations occurring in the region 960 to 1650 cm^{-1}, and the polarization characteristic is also found to the same over the entire contour of the broadened lines. The Raman line at 1240 cm^{-1} has a width of nearly 40 cm^{-1}. Though the known centro-symmetric structure of α-*MAC* would in principle, if correlation coupling is strong, lead to the Raman active frequencies being different from the infrared band frequencies, we believe that the difference of 23 cm^{-1} between $\nu_{11}(E)$ frequencies found in Raman scattering and absorption is due to the width from hydrogen bonding. This view is further supported by the fact that in the aqueous solution the same NH_3 rocking mode has a higher frequency *viz.*, 1280 cm^{-1}. Nearly all the observed frequency shifts in the Raman spectrum of α-*MAC* agree within experimental error with the infrared absorption maxima and thus there is no definite spectroscopic evidence for the coupling between the vibrations of the two $CH_3N^+H_3$ groups in the unit cell. The absence of correlation coupling effects make the assignments easier and the assignments have been indicated in Table I with the same notation as Waldron[4] and Theoret and Sandorfy.[13] Contrary to what has been generally observed in other primary and secondary amines and in ammonium salts we did not find any Raman lines either in the crystal or solution in the ' indicator band ' region. Due to the presence of a mercury line in the region of $\nu_3 (A_1)$, the corresponding Raman line could not be measured. In the aqueous solution the Raman line at 1626 cm^{-1} and the shift of the water band from its normal value and its width are presumably due to the hydrogen bonding and the stretching frequency also shows a downward shift to 3447 cm^{-1}.

It is in the region of the valence vibrations of the $^+NH_3$ and CH_3 groups *viz.*, 2800 – 3000 cm^{-1} that we find it necessary to suppose that a Fermi resonance between the *C-H* stretching frequency and the second harmonic of the *C-H* bending vibrations must be the reason for the presence of intence Raman lines. Edsall and Scheinberg[2] found that on *N*-deuteration the Raman lines in this region hardly showed any shift and came to the same conclusion. A comparison of the frequencies in the solid state and solution also favours this interpretation only, as one should find some broadening or shifting in the case of $^+NH_3$ vibration mentioned earlier. The Raman line at 2826 cm^{-1} corresponding to the infrared band at 2840 cm^{-1} cannot arise from the fundamental valence vibrations, though a similar line observed at 2820 – 2850 cm^{-1} in ammonium chloride (R. S. Krishnan)[14] has been attributed to an overtone of the fundamental frequency of the NH^+_4 ion (L. Couture and J. P. Mathieu)[15]. But in the present case the 2826 cm^{-1} Raman line is unaffected by deuteration and has therfore been attributed to the CH_3 group vibrations rather than those of the NH_3 group (Table I).

The crystal structure data indicate an $N \cdots Cl$ distance of 3.2 Å and according to the correlation curve given by Nakamoto, Margoshes and Rundle[16] the corresponding *N-H* stretching frequency should occur around 3050 cm^{-1} and in this case also the Raman line at 3020 cm^{-1} cannot be attributed to the $^+NH_3$ group as it is unaffected by deuteration. It is therefore concluded that the valence vibrations of the $^+NH_3$ group give rise only to a very broad and weak band superimposed on the lines due to the *CH* vibrations. This would account for the observed intensity distribution in the Raman spectrum.

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TABLE I

Raman Shifts and Infrared Absorption Maxima of Methylammoium Chloride (in cm^{-1})

Solid State Raman shifts	Aqueous solution Raman shifts	Solid State I. R. maxima	Assignments
54 (w)			
87 (w)			
184 (w)			
		664 (m)	
960 (w)		959 (m)	CH_3 rocking ν_{12} (E)
1000 (w)	1000 (P)	1003 (w)	C-N stretch ν_5 (A_1)
1240 (br)	1280	1263 (w)	NH_3 rock ν_{11} (E)
		1248 (w)	CH_3 sym. bend ν_4 (A_1)
1439 (v.w)	1432 (D)	...	
1465 (w)	1469 (D)	1464 (w)	CH_3 asym. bend ν_{10} (E)
		1538 (str.)	NH_3 sym. bend ν_3 (A_1)
		1575 (str.)	NH_3 asym. bend ν_9 (E)
	1626 (br)		ν (H_2O)
		1905 (v.w.)	$2\nu_{12}$
		2212 (v.w,)	(959 + 1263) $\nu_{11} + \nu_{12}$
		2480 (v.w.)	$\nu_3 + \nu_{12}$
		~ 2565 (v.w.)	$\nu_5 + \nu_9$
		~ 2770 (m)	$\nu_3 + \nu_{11}$
2783		...	$\nu_3 + \nu_{11}$
2826	2838 (str.) (P)	~ 2480 (m)	$2\nu_4$, $\nu_4 + \nu_{10}$
2904	2914 (str.) (P)	2917	ν_2 (A_1)
2963	2980 (v. str. (D)	2980 (str.)	(A_1) CH vibrations
3020	3040 (str.) (D)	3080 (str.)	(E)
	3447 (br)		ν (H_2O)

w : weak m : medium p : polarised
v.w. : very weak str : strong d : depolarised.

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