

ON THE RAMAN SPECTRA OF CHLORO AND BROMO-
ACETYL CHLORIDE IN THE SOLID STATE.

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Plate I

ABSTRACT. The Raman spectra of chloro- and bromo-acetyl chloride in the liquid and solid states as well as the polarisation of the Raman lines of these liquids have been studied. It is observed that in the liquid state the former compound yields a smaller number of lines than the latter, which again gives much more lines than those expected theoretically. In the latter case some of the prominent lines disappear in the solid state, while in the case of chloro-acetyl chloride no such change takes place. New lines in the low frequency region appear in the solid state in both the cases. The changes observed in the case of bromo-acetyl chloride are ascribed to the formation of strongly associated molecules in which the C-Cl and C-Br valence forces in the molecule are affected in the liquid state. It is pointed out that in the case of propyl bromide also similar explanation was offered by previous workers.

INTRODUCTION

The Raman spectra of acetyl chloride and acetyl bromide have been studied in the liquid as well as in the solid state by Bishui (1948a). It has been reported that all the prominent Raman lines due to the liquid state are also present in the solid state. It has, therefore, been concluded that there is no rotational isomers in these liquids. It has been argued by him that the presence of two extra lines below 1200 cm^{-1} in the Raman spectra of each of the substances may be due to the formation of associated groups of molecules in the liquid and solid states of the substances. In order to get definite information regarding the structure of molecules in these cases two halogen substituted derivatives of acetyl chloride have been chosen in the present investigation. The Raman spectra of chloro-acetyl chloride and bromo-acetyl chloride in the liquid and solid states have thus been studied in order to find out the difference in the Raman spectra due to the two states. Incidentally, the Raman spectra of bromo-acetyl chloride was not studied by any previous worker and it was not known how the Raman spectra is affected when the chlorine atom attached to the CH_2 group in acetyl chloride is replaced by a bromine atom. The polarisation of the Raman lines due to these two liquids has also been studied in order to get information regarding the symmetry of the molecules.

EXPERIMENTAL

The liquids from Kahlbaum's original packings were obtained from old stock of this laboratory and were redistilled in vacuum. The method for studying the Raman spectra of the compounds at low temperatures was the same as that described by Bishu (1948b). A long pyrex glass tube containing the distilled liquid was held in the vapour of the liquid oxygen which was constantly being evaporated from the lower portion of the transparent Dewar vessel. The level of the liquid oxygen in the transparent Dewar vessel was maintained at a position about a centimetre below the bottom of the tube containing the distilled liquid. Evaporation of the liquid oxygen was frequently accelerated by pumping out the cold vapour above the surface of the liquid oxygen with a Cenco Hyvac pump. A pentane thermometer, which passed through a cork fitted into the mouth of the transparent Dewar vessel, was held in the vapour of the liquid oxygen to record the temperature. The solidification of the experimental liquid took place slowly and a semi-transparent solid mass of the substance was obtained. Light from two vertical mercury arcs, condensed by two six inch glass condensers, was focussed on the substance from opposite sides.

A Fuess glass spectrograph, having a dispersion of 13.5 \AA per mm. in the region of 4046 \AA , was used in this investigation. A blue-violet glass filter was placed in the path of the incident light in order to diminish the continuous background in the blue-green region. The polarisation of the Raman lines due to the liquids was studied in each case by photographing simultaneously the vertical and horizontal components of the scattered light with the help of a double image prism. Light from a mercury arc, focussed by means of a glass condenser, was used as the incident light in these cases.

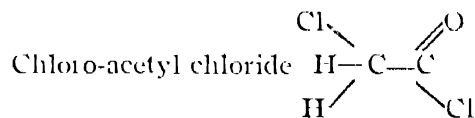
RESULTS AND DISCUSSIONS

The spectrograms for the liquid and the solid state are reproduced in Plate I. The results are given in Tables I and II. The results reported by some previous workers have been given in the first column in the case of chloro-acetyl chloride only. The data for the solid obtained in the present investigation are given in the last column. The letters *e*, *k*, *i*, *c* represent exciting lines in Kohlrausch's notation. *P* means $\rho \ll 6/7$ and *D* means $\rho = 6/7$. The approximate visually estimated intensities are given in parentheses.

It can be seen from Tables I and II that the numbers of Raman lines, having frequency shifts less than 1000 cm^{-1} , observed in the case of the two liquids are quite different from each other. The results reported by Cheng (1934) in the case of chloro-acetyl chloride show that there are seven Raman lines in the region mentioned above of which the line 899 cm^{-1} is extremely weak. With the exception of this line all the other lines have been observed in the present investigation. It has further been observed that all these lines

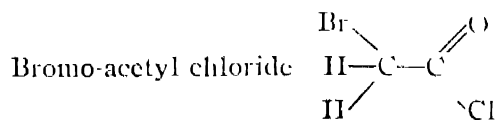
Raman Spectra of Chloro- and Bromo-acetyl Chloride 3

TABLE I



Liquid at 30°C		Solid at about -150°C
Hua-chi-cheng (1934)	Present authors	Present authors
304-(10) c±, k, i, f	300-(5) c±, k, c, P	480-(0) k
452-(10b) c±k, i, c	453-(6) c±, k, c, P	300-(1) c, k
562-(1) c	500-(0b) c, k, P	459-(3) c, k
719-(3b) c, k	712-(1b) c, k, c, P	565-(0) s) c, k
784-(10) c±k, i, c	780-(6) c, k, P	724-(1) c, k
899-(00) c, k ?		780-(5) c, k
970-(5) c	970 (0b) c, k, P	X
1179-(1) c, k		
1400-(2) c, k	1402-(2b) c, k, D	1400-(0) c
1800-(2) c	1810-(2b) c, P	1800-(0) c
2050-(10) c, k, i	2052-(6) c, k, P	2040-(6) c, k
2097-(5) c, k	2092-(1) c, k, P	2092-(2) c, k

TABLE II



Liquid at 30°C	Solid at about -150°C
Present authors	Present authors
150-(1) D	40-(0) k
188-(2b) c, D	170-(0) c
250-(3) c±, k, P	258-(3) c, k
297-(0), e, P	297-(1) c
363-(2) c, k, D	V
449-(5) c±, k, P	452-(5) e, k
490-(6) e, P	V
526-(3) e, k, P	672-(0) c
704-(1) c, k, P	735-(5) c, k
730-(5) e, k, P	
953-(0) c, k, P	
1303-(2) c, k, D	1385-(0) c, k
1816-(3b) c, P	1812-(0) c
2056-(5) c, k, P	2680-(8) e, k
3014-(1) c, k, P	3014-(2) c, k

are polarised. No data for bromo-acetyl chloride are available and it seems that this liquid was not investigated before. The number of Raman lines, having frequency shifts below 1000 cm⁻¹, observed in this case is eleven. Three of these lines are observed to be totally depolarised. The Raman

lines in this region are given by the vibrations of the group $\text{X}-\text{C} \begin{array}{l} \text{=} \text{O} \\ \diagdown \\ \text{Cl} \end{array}$

where X stands for Cl and Br in the two cases. It is thus evident that when there are two Cl atoms in this group at the two ends the number of Raman lines is reduced. Ordinarily, according to the group theory this group having only a plane of symmetry would yield altogether nine Raman lines of which seven are polarised and two are totally depolarised as can be seen from Table III.

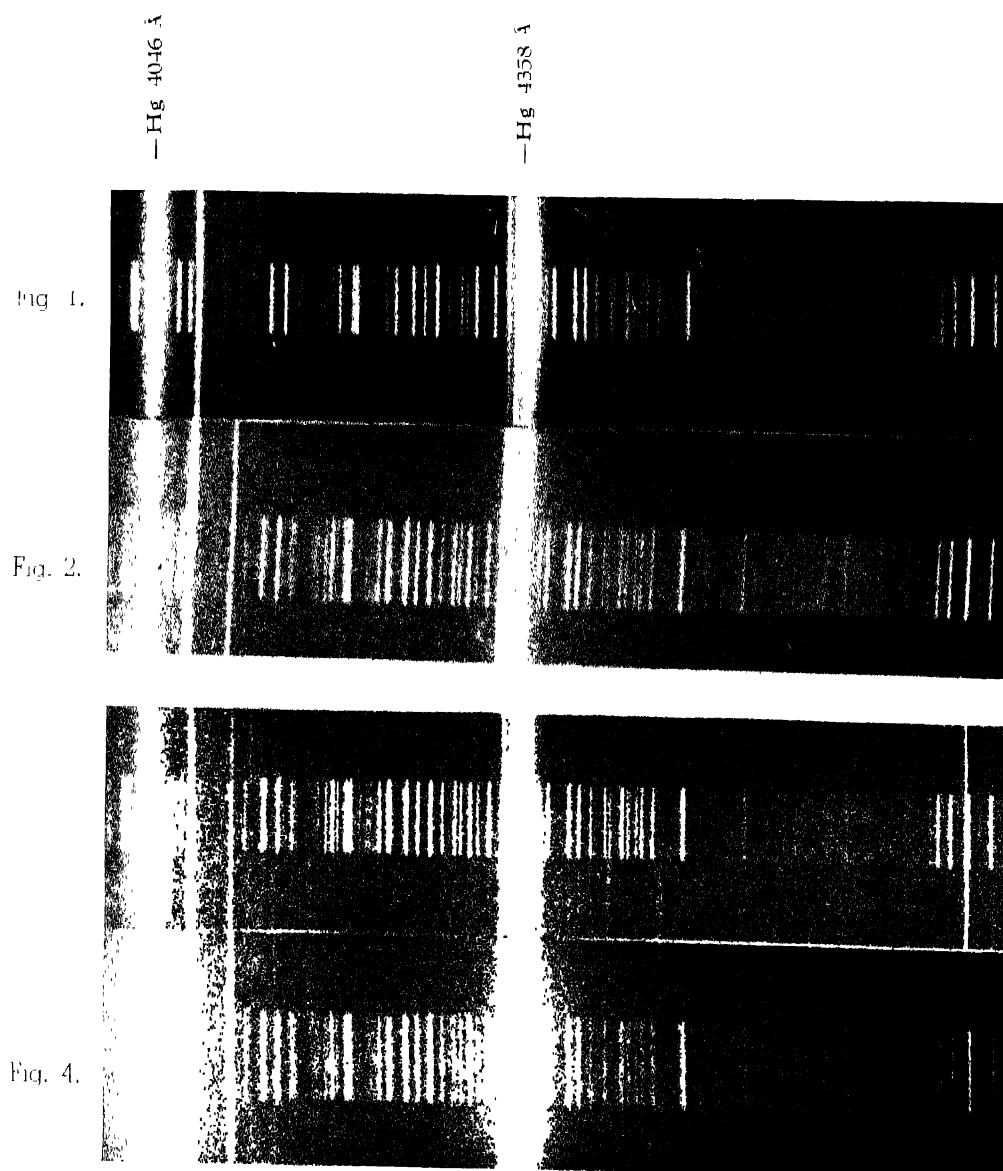
TABLE III

C.	E	σ	n'	T & R	Raman effect.
Λ'	1	1	10	3	7 P
Λ''	1	1	5	3	2 D
UR	5	5			
h_1, λ_1	15	5			
h_2, ψ_1	9	5			

It is thus evident that in the case of chloroacetyl chloride the number

of Raman lines due to the group $\text{Cl}-\text{C} \begin{array}{l} \text{=} \text{O} \\ \diagdown \\ \text{Cl} \end{array}$ actually observed is less than

that expected theoretically and that the totally depolarised lines are absent. On the other hand in the case of bromoacetyl chloride the number of such lines actually observed is much more than that expected theoretically. This peculiar difference in the behaviour of the two molecules can be explained on the assumption that in the case of chloroacetyl chloride the selection rules for the appearance of the Raman lines due to the vibration of the group $\text{Cl}-\text{C}-\text{C}-\text{Cl}$ is not affected very much by the presence of the divalent oxygen atom attached to one of the carbon atoms. In that case this group of four atoms would have a centre of symmetry and would yield only three lines, all polarised, and due to the presence of the oxygen atom three more lines, all polarised, would be expected. In other words, out of the nine lines, mentioned in Table III, only six would be observed and besides the two depolarised lines mentioned therein another line, due to the antisymmetric valence oscillation of C-Cl group, would be absent. Taking into account the line at 1810 cm^{-1} due to the C=O oscillation, it is found that



Raman Spectra

Fig. 1.—Chloroacetyl Chloride at about + 30°C.

Fig. 2.— " " " " - 160°C.

Fig. 3.—Bromoacetyl Chloride at about + 30°C.

Fig. 4.— " " " " - 160°C.

besides these lines an extra line appears in the Raman spectrum of this substance in the liquid state. This line may be due to the association of the molecules.

In the solid state at the low temperature the intensity of the line 1810 cm^{-1} diminishes appreciably and its frequency also diminishes by 8 wave numbers. The line 560 cm^{-1} becomes sharper in the solid state and an extra line at 48 cm^{-1} appears in the neighbourhood of the Hg line 4046 \AA . This latter line is quite sharp and considering the complicated structure of the molecule it is difficult to ascribe this line to rotational oscillation of the molecule in the lattice as suggested by Kastler and Rousset (1941) in the case of benzene and naphthalene.

In order to explain the appearance of many extra lines in the case of bromoacetyl chloride the hypothesis of co-existence of rotational isomers in the liquid state could be put forwards as was done in the case of other dihalogen derivatives of ethane by Mizushima *et al* (1936). There is, however, a serious difficulty in applying the same hypothesis in the present case, because if the rotational isomers could be present in the liquid state of bromoacetyl chloride they would also be present in the case of chloroacetyl chloride, but actually it has been shown above in the latter case there is strong evidence for the existence of only one type of the molecule. Hence in the case of bromoacetyl chloride also rotational isomers cannot be present. Probably in the latter case the molecules are strongly associated and on solidification due to uniform distribution of the molecules some of the virtual bonds become loosened and the corresponding Raman lines disappear. Such an explanation has been offered in the case of propyl bromide by Bishui (1948c). The remarkable changes observed in the Raman spectrum of bromoacetyl chloride with the solidification of the substance can thus be explained. The changes observed are rather large, because the strong lines 363 and 526 cm^{-1} disappear and the line 207 cm^{-1} becomes more intense in the solid state. Also the frequency shift of the line 2956 cm^{-1} , due to C-H oscillation, increased to 2980 cm^{-1} in the solid state and the intensity of the line 1812 cm^{-1} diminishes appreciably. The changes are not observed in the case of chloroacetylchloride probably because the virtual attachment of chlorine atom to any of the two carbon atoms produces the same change in the C-Cl frequency in both the groups to the same extent. A comparison of the Raman spectra of the liquid and solid states of chloro-and bromo-acetyl chloride thus seems to support the hypothesis put forward by Bishui (1948c) regarding the changes occurring in the Raman spectra of propyl bromide with the change of state.

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