

ON THE POLARISATION OF RAMAN LINES OF FORMIC ACID, AND FORMATE AND TRICHLORACETATE IONS.

BY JAGANNATH GUPTA.

(Palit Research Scholar in Chemistry.)

(Received for publication, July 4th, 1936.)

(Plate XIX.)

ABSTRACT.—The degrees of depolarisation of the prominent Raman lines of formic acid and of sodium formate and sodium trichloracetate in aqueous solutions have been measured, using a double-image prism to record the two components simultaneously and determining the relative intensities of the components with the help of blackening-log (intensity) curves. It is found that the degree of depolarisation of the line 1398 cm^{-1} of formic acid is .41, which is much greater than that of either the line 1353 cm^{-1} of sodium formate or the line 1330 cm^{-1} of sodium trichloracetate. This fact indicates positively that the origin of the line 1353 cm^{-1} of sodium formate is different from that of the line 1398 cm^{-1} of formic acid. The agreement between the values of ρ of the line 1353 cm^{-1} of sodium formate solution and of the line 1330 cm^{-1} of sodium trichloracetate solution goes to show that the two lines owe their origin to the same mode of vibration of the carboxyl group.

INTRODUCTION.

It is well known that the degree of depolarisation ρ , of a Raman line is an unmistakable guide to the understanding of the vibration which causes the appearance of the line. In spite of the fact that the measurement of ρ is exceedingly difficult, the polarisations of the Raman lines of a large number of substances have been successfully investigated by several workers using the accurate methods of photographic photometry of spectral lines, and in those cases where the results can be interpreted, it has been found that they are in agreement with those expected from the theoretical point of view.

Attempts to interpret and make a comparative study of the Raman spectra of carboxylic acids and those of their metallic salts in solution have been made only recently. An examination of the Raman spectrum of trichloroacetic acid led Kohlrausch¹ to suggest for it the structure as proposed by Hantzsch² for the fatty acids. A marked difference between the spectrum of a pure acid and that of its metallic salts in solution led Psychès³ to put forward the view that the angle between the two (C—O) bonds increases in solution when the salt is ionised. All these views have been discussed and extended by the present author in a previous paper.⁴

It is evident that the correctness of the hypotheses mentioned above can be easily tested by making a comparative study of the values of ρ , the degree of

depolarisation, of the Raman lines of carboxylic acids and their metallic salts. Sufficient data for this purpose are not available. The values of all the Raman lines of formic acid reported by Parthasarathy⁵ seem to be too high; for instance in the case of the band at 180 cm^{-1} the value of ρ as reported by him is 1.4, i.e., the line exhibits anomalous depolarisation; but theoretically, values greater than $6/7$ can never be expected and it has been definitely shown by Bür⁶ that such anomalous depolarisation of Raman lines does not really exist. For this reason, measurements of the degrees of depolarisation of the Raman lines of formic acid, sodium formate solution and sodium trichloroacetate solution were undertaken by the present author. The results have been described and discussed in the present paper.

EXPERIMENTAL.

The straight portion of a quartz mercury arc cooled by breeze was focussed with a big condenser on a Wood's tube placed parallel to the arc. Some portions of the tube were painted black to avoid reflections. At the centre of the plane window of the Wood's tube a rectangular portion, about 4 mm. square, was left unpainted to transmit the scattered light. The scattered light was allowed to pass through a double image prism of the Wollaston type which resolved the scattered light into two components. The components were then focussed simultaneously with a short-focus lens so that the two images of the aperture were formed on the slit of the spectrograph, one being vertically above the other. Every precaution was observed to avoid any stray light from anywhere, and to keep the Wood's tube, the prism, the lens and the collimator axis in perfect alignment. The two components of the scattered light were thus simultaneously photographed with a Hilger two-prism glass spectrograph on Ilford Golden Isozenith plates. Intensity marks were then taken on the plate by varying the width of the slit of the spectrograph and using a standardised tungsten ribbon lamp as the source of continuous radiation for this purpose. The scale attached to the slit of the spectrograph had been previously calibrated with the help of a comparator. Microphotometric records were taken of the spectrograms with a self-registering Moll microphotometer and the ratio of the intensities of the two components of each Raman line was determined by finding the respective intensities from the blackening-log (intensity) curves for the corresponding wave-lengths. The corrections for the continuous background were carefully made. For this purpose, for any Raman line the total density produced by the line and the continuous background together and that for the latter alone were measured, and with the help of the blackening-log (intensity) curve, the corresponding total intensity and the intensity of the continuous background alone were separately determined. The intensity of the Raman line was then obtained by subtracting the latter from the former.

In the experimental arrangement described above there are two main sources of error, one due to lack of transversality of the incident beam and the other due to loss of intensity of the vertical component of each Raman line owing to reflections at the surfaces of the prisms inside the spectrograph.* In order to correct for these errors, the depolarisation factors of the Raman lines of carbon tetrachloride were determined with exactly similar experimental arrangements as used for the substances mentioned above. The observed value of ρ for the line 459 cm^{-1} of carbon tetrachloride was then compared with the accepted standard value reported by previous workers and the correction factor was calculated. It was found that when $\cdot06$ was subtracted from the observed value of ρ of each of the Raman lines, the values so obtained agreed closely with those reported by Cabannes and Rousset.⁷ The corrected values are tabulated below for comparison :

$\Delta \nu$	218	314	459	776
ρ { I	$\cdot83$	$\cdot79$	$\cdot05$	$\Delta 6/7$
ρ { II	$\cdot82$	$\cdot79$	$\cdot05$	$\cdot88$

I Cabannes and Rousset.

II Author.

This correction factor was therefore used for getting the true values of ρ of the Raman lines of the substances under investigation.

RESULTS.

Degrees of Depolarisation of Raman Lines (corrected values). Exciting Line, Hg. 4358 Å.

Formic acid.		Sodium formate solution.		Sodium trichloracetate solution.	
$\Delta \nu$.	ρ .	$\Delta \nu$.	ρ .	$\Delta \nu$.	ρ .
189	depolarised			434	$\cdot08$
673	$\rho > \cdot8$			838	depolarised
	$\cdot7$				$\rho > \cdot7$
1398	$\cdot41^\dagger$	1352	$\cdot15^\dagger$	1330	$\cdot24$
1672	$\cdot41$		$\cdot17$	1667	depolarised
	$\cdot17$				$\rho > \cdot7$
		2735	$\cdot7$		
		2834	$\cdot47$		
2963	$\cdot25$				

* The error from the latter source was very small, because the experimental arrangement was such that both the components were inclined to the vertical at about 45° . The particular Wollaston prism supplied by the manufacturers is such that when the separation of the two rays is in the vertical direction, the principal plane is inclined to the vertical at an angle of about 45° . This angle was determined and the incident beam was sent in this direction in the actual experiment.

† Excitation by 4047 Å Hg line.

DISCUSSION OF RESULTS.

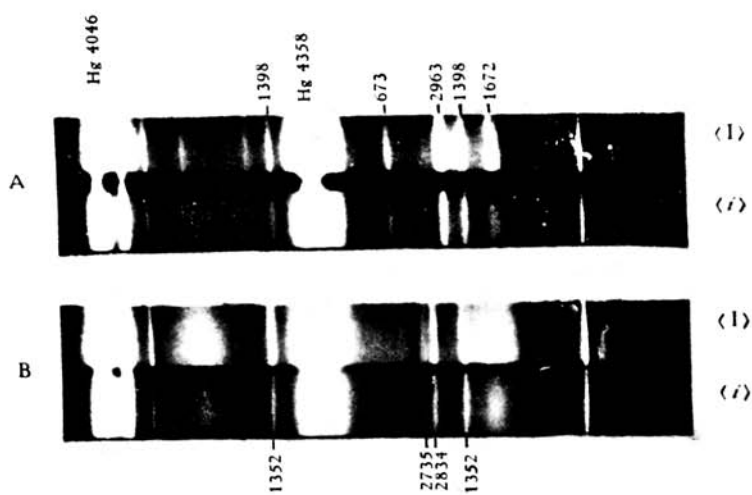
It can be seen from the results given above that the line 1352 cm^{-1} in sodium formate solution is much more polarised than the line 1398 cm^{-1} in pure formic acid. In a paper on the Raman spectra of formic acid and metallic formates, Venkateswaran³ attributed to the line 1353 cm^{-1} of sodium formate the same origin as the line 1398 cm^{-1} of pure formic acid, viz., the deformation oscillation of C-H in the HCO group. Objections to this view were put forward by the present author in a previous paper⁴ from a comparative study with the Raman spectra of other acids like trichloroacetic and its sodium salt in solution, in which the alternative view was put forward that the line has its origin in the inner

oscillation of the $\left(-\text{C}\begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}\right)^-$ group.

If Venkateswaran's views are accepted to be correct and the line 1353 of sodium formate is assumed to be the same line as 1398 of formic acid,—displaced only under the influence of the metallic ion,—it follows that the depolarisation values of the lines must be identical, since the value of ρ depends only on the mode of vibration. The essentially different values of ρ of the lines 1398 of formic acid and 1353 of sodium formate solution as shown in these depolarisation measurements show that they cannot have the same origin.

On the other hand, the agreement of the value of ρ for the line 1353 of sodium formate with that of the line 1330 of sodium trichloroacetate is more satisfactory, and the small difference in the values can be attributed to the presence of some continuous background in the spectrum of sodium trichloroacetate solution, which could not be removed. The *m*-dinitrobenzene filter may have also effected a partial depolarisation of the lines of sodium trichloroacetate solution. The essentially high degree of polarisation of the line 1330 cm^{-1} is however evident, even under such experimental difficulties. This agreement in the two values goes a long way to show that the two lines are originated from the same mode of vibration.

The next question that arises is whether the line 1353 in sodium formate or the line 1330 in sodium trichloroacetate is due to the symmetric or to the anti-symmetric vibration of the $\left(-\text{C}\begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}\right)^-$ group. In the case of the acids, it was suggested by Kohlrausch that the line in the region of 1650 cm^{-1} is due to the symmetric vibration, and that in the region of 1400 cm^{-1} to the antisymmetric vibration of the $\left(-\text{C}\begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}\right)\text{H}$ group. This view is supported by the values of ρ observed in the case of formic acid, where the line 1672 cm^{-1} is highly polarised. The reverse, however, seems to be true in the case of the salts in solution. The



Polarisation of Raman Lines.

A → Pure formic acid.

B → Sodium formate solution in water.

(1) — Strong component. (i) — Weak component.

exceedingly sharp and intense nature of the line in the region of 1350 cm^{-1} as compared to the broad and diffuse nature of the line near 1650 cm^{-1} in the solutions of the salts of the acids, naturally suggests that the former line is caused by the symmetric oscillation of the ionised carboxyl group $\left(-\text{C}\begin{matrix} \text{O} \\ \text{O} \end{matrix}\right)^{-}$.

This view again is definitely verified from the depolarisation measurements, as the line 1330 cm^{-1} of sodium trichloroacetate is shown to be highly polarised and the line 1650 , depolarised. Such a reversal in the values of ρ is not inexplicable since it has been suggested by Peychès and confirmed from X-ray analysis by Hendricks and Jefferson⁹ in the case of ammonium oxalate that in an ionised carboxyl group, the angle between the two C-O bonds assumes a much greater value than in the pure acid. Such a large increase in the angle will profoundly alter the shape of the ellipsoid representing the change of polarisability, upon which the value of ρ ultimately depends.

The difference in the values of ρ of the lines 2735 cm^{-1} and 2834 cm^{-1} seems to be significant. Since one of the lines is almost completely depolarised and the other is partially polarised, it appears that these two lines may be due to different modes of vibration of the (C-H) group. Since there is only one line at 2963 cm^{-1} in formic acid due to the valence oscillation of the CH group, while there are two lines having different degrees of depolarisation in the case of the formate ion, it is quite probable that in the latter case the C-H binding has undergone some changes in orientation with respect to the axis of the molecule. It is suggested that the change shown below diagrammatically may have taken place,—



This may represent the stage of the ions which have not yet undergone complete prototropic rearrangement as suggested by Ray and Sarkar¹⁰ and discussed by the present author previously.⁴

In conclusion, the author wishes to express his respectful thanks to Sir P. C. Rây for his kind interest in the work and to Prof. D. M. Bose for providing the author with facilities to work in the Palit Laboratory of Physics. The work was carried out under kind guidance of Dr. S. C. Sirkar, to whom also the author's best thanks are due.

PALIT CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

R E F E R E N C E S .

- ¹ Kohlrausch, *Z. Phys. Chem. B*, **22**, 359 (1933).
- ² Hantzsch, *Ber. Deut. Chem. Ges.*, **50**, 1422 (1917).
- ³ Pechin, *Bull. Soc. Chim*, **2**, 2195 (1935).
- ⁴ Gupta, *Ind. J. Phys.*, **10**, 117 (1936).
- ⁵ Parthasarathy, *Ind. J. Phys.*, **6**, 287 (1931).
- ⁶ Bär, *Nature*, **120**, 525 (1932).
- ⁷ Cahannes and Roussel, *Ann. de Physique*, **19**, 229 (1933).
- ⁸ Venkateswaran, *Proc. Ind. Acad. Sci.*, **2**, 615 (1935).
- ⁹ Hendricks and Jefferson, *J. Chem. Phys.*, **4**, 102 (1936).
- ¹⁰ Ray and Sarkar, *Nature*, **137**, 495 (1936).

Corrigendum: Substitute the following figure in place of figure 3, plate XVIII
(Basu & Hussain) facing page 268 of this volume. Also put 68 in
place of 64 in reference No. 4 of the same paper.

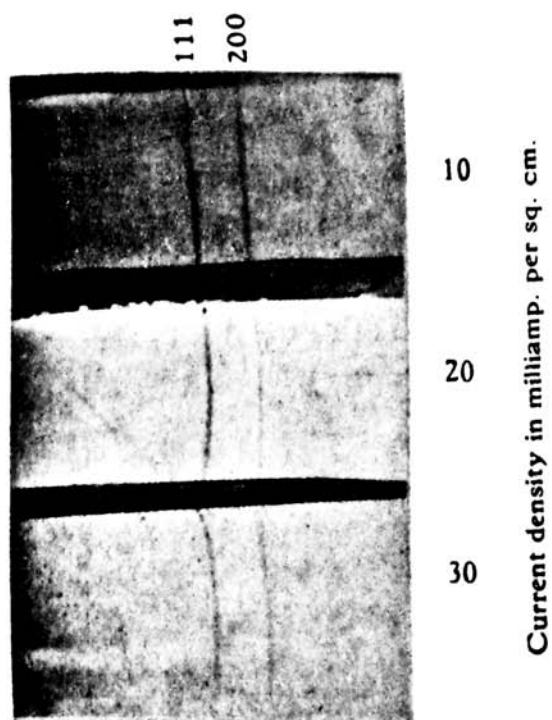


Figure 3