EFFECT OF COMPLEX FORMATION ON THE INTENSITIES OF RAMAN LINES

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ABSTRACT. On adding 5N ammonium nitrate to 13N nitric acid, $d\nu = 1300$ of nitric acid is found to decrease instead of increasing in intensity contrary to what is required by the law of mass action. To understand this, it is postulated that a complex like HNO_3NO_3 is formed and it is surmised that when a complex is formed the bond stretching oscillation of a Raman line is decreased while it is known that the corresponding infra-red line decreases in intensity, during the formation of a complex. $d\nu = 1680$ of acetic acid also is found to behave in a similar way.

INTRODUCTION

In recent years (Coggeshall, 1950 and Venkataramaiah and Puranik, 1962) it has been observed that the intensity of the line corresponding to any bond which is attached to another molecule due to hydrogen bond formation is increased. In fact, quantitative estimates of the intensities as related to the shift in the frequency of the bond due to hydrogen bond formation have been made. Now we report a few cases to say that the corresponding Raman line decreases in intensity.

Nitric acid: One of us (1943) reported many years back that when to a solution of bisulphate a sulphate is added, $d\nu = 1040$ cm^{-1} corresponding to the HSO_4 ion decreases in intensity, contrary to the law of mass action, while addition of an acid brightens it as expected. Similar observation is made in a solution of nitric acid using NH_4NO_3 and $HClO_4$ as sources of NO_3 and H ions.

TABLE I

	I(1050)	I(1300)
NH₄NO₃ (5N)	7.0	—
HNO₃ (13N)	3.6	6.2
HNO₃ (13N)+ NH₄NO₃ (5N)	5.8	5.2
HNO₃ (13N)+ HClO₄ (5N)	1.5	7.2

Table I shows that I(1300). belonging to HNO_3 molecules decreases in intensity from pure acid to nitrate mixture but brightens up in $HClO_4$ mixture, similar to what is observed in the case of bisulphates. The microphotometric records demonstrate the effect clearly. (Fig. I).
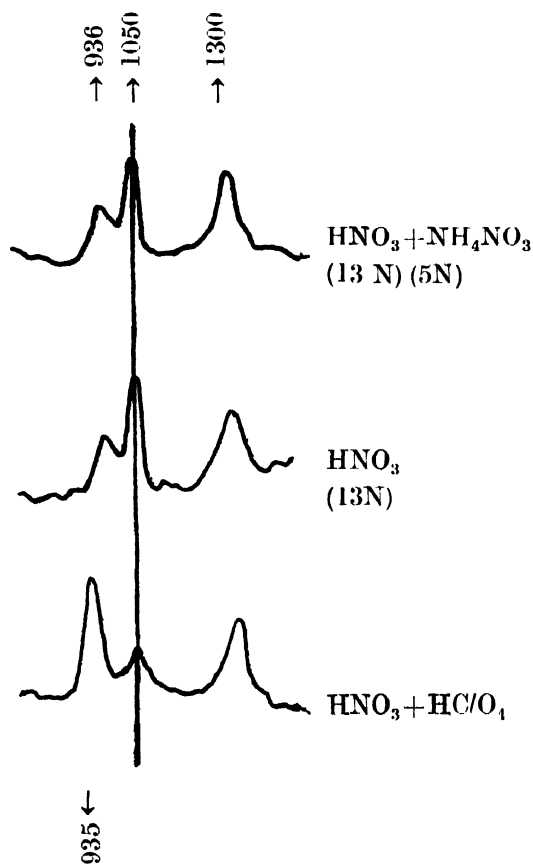

Fig. I

In order to see whether the same result is reflected by the conductitivity data, electrical conductivity of these mixtures is measured and the data given in

TABLE II

1	2	3	4	5	6	7	8	9	10
Temp °C	HNO_3	NH_4NO_3	Mixture	2+3 -4	5/2+3	$HClO_4$	Mixture	2/7 - 3	9/2+7
2	531.0	102.5	390.9	242.6	38.3%	355.6	377.8	508.8	57.4%
25	759.3	161.7	584.1	334.9	36.4%	515.2	554.5	720.0	56.5%
50	946.1	224.0	814.3	355.8	30.4%	642.1	692.9	895.3	56.4%

Conductivity in millimhos of nitric acid and its mixtures with ammonium nitrate and perchloric acid. Columns 6 and 10 show percentage decrease of conductivity in the mixtures.

Table II. Though, at these concentrations it is not possible to relate conductivity to the number of ions, qualitatively, it can be seen that nitrate ion also supresses conductivity like the hydrogen ions, contrary to Raman effect data.

We are tempted to suggest formation of complex like NO_3HNO_3 with a hydrogen bond between NO_3 and HNO_3. This explains why NO_3 helps suppression of conductivity to a large extent. The microphotometric records show that there is a line at $dv = 936$ belonging to HNO_3 molecules stronger in the nitrate mixture than in pure acid. This probably means that the decrease in the intensity of $dv = 1300$ is not due to reduced number of HNO_3 molecules but to the specific intensity (intensity per molecule) of the line decreasing due to hydrogen bond formation.

TABLE III

Solution	$dv = 446$	610	872	893	1270	1368	1680
Acetic acid pure	10	32	100	29	13	13	19
(2N) acid	15	32	100		15	20	52
Sodium acetate (2N)	13	17		100	37	70	0
acid and salt mixture 2N each	26	37	100	95	37	60	40

Acetic acid : A similar experiment is performed in mixtures of acetic acid and sodium acetate and the results given in Table III. The intensities are reduced to $dv = 872$ taken as 100. It shifts to 893 in the spectra of salts. In the mixture, we see the two lines well separated. We want to point out to the large reduction in the intensity of $dv = 1780$ attributed to $C = 0$ (Koteswaram, 1940) from 2N solution to pure acetic acid where dimers are known to form. Its reduction in the mixture is probably due to a complex like $H_3CCOOH - OOCC-CH_3$ with hydrogen bond formation.

Sulphuric acid : 100% sulphuric acid contains about 18 moles per litre while water contains 54 moles. Yet, Raman spectrum of sulphuric acid does not show any OH band of detectable intensity, though water with 1/3 of the time given for the acid shows the band very well. It should be mentioned in this connection, however, that C. S. Venkateswaran (1938) reported a faint band at $dv = 2794$ to 3172 for sulphuric acid. We are tempted to suggest that molecules in pure sulphuric acid are so intimately connected by hydrogen bonds that OH bond is very much reduced in intensity.

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