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CHANGE IN THE SHAPE OF A MOLECULE DURING THE FORMATION OF HYDROGEN BOND

N. RAJESWARA RAO AND K. V. RAMANAIAH

PHYSICS DEPARTMENT, OSMANIA UNIVERSITY, HYDERABAD

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Plate V

ABSTRACT. Evidence is found to show that C=O bond frequency $d\nu = 1710$ of monochloacetic acid, the total symmetric line $d\nu = 910$ of sulphuric acid and the total symmetric line 1050 of the nitrate ion in solution are found to decrease on depolymerisation due to heating, contrary to expectation. This goes against the assumptions usually made that the bond in question is unaffected by the presence of the other atoms in the molecules and the other molecules in the liquid. It is surmised that the molecules change their shape during the formation of a complex. The structure of the nitrate ion is pyramidal in solution at low temperature and it becomes plane on heating. This is taken to be a direct evidence for crystalline nature of hydration of ion in solution postulated by Lengyel.

INTRODUCTION

It is well known* that during the formation of a complex by hydrogen bond, the stretching frequency of the bond, to which the proton from the neighbouring molecule is attached, is decreased. This change in the frequency is calculated in a number of cases, on the assumptions that (1) the bond in question is not affected by the other atoms in the molecules and (2) the molecules that are joining to form the complex are not influenced by the others in the liquid. We have, now gathered evidence to show that these assumptions are not quite justified.

1. Monochloracetic acid : One of us (1944) reported on the changes in the $C = O$ stretching frequency of this acid at various concentrations and temperatures. At $10.5N$, it shows a sharp maximum at $d\nu = 1710$. With dilution, a component appears at $d\nu = 1617$ which increases in intensity while the peak at $d\nu = 1710$ decreases. On heating the solution from 30°C to 80°C, also, the component at 1617 brightens up. As usual, $d\nu = 1710$ is attributed to a dimer and $d\nu = 1617$ to an unattached molecule, the hydrogen bond formation increasing the frequency contrary to general expectation. Most of the studies on complex formation by the application of Raman Effect depend on the shift of this line to lower frequency as, for instance, in the case of acetic acid (Kotaswaram, 1944), and trichloroacetic acid (N. R. Rao, 1943). Obviously, the $C = O$ bond should not be regarded as if it is isolated.

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* Coggshall, 1950, Venkataramainah & Puranik, 1962

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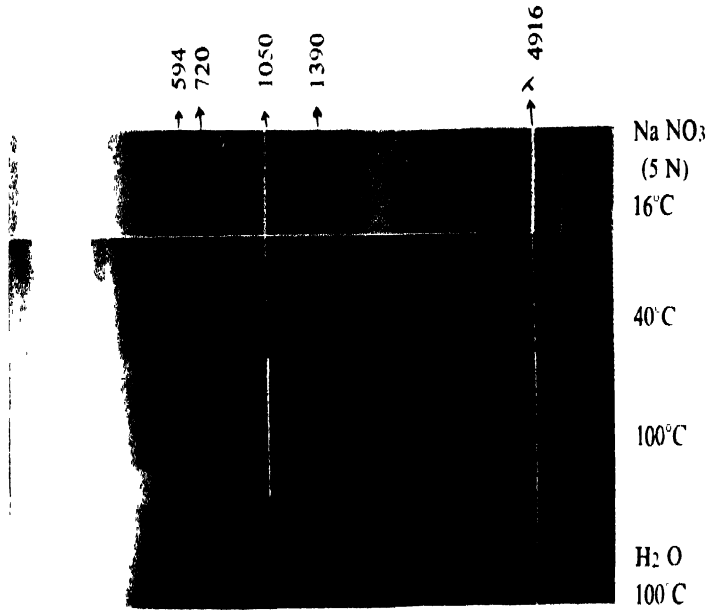

Raman spectra of nitrates at various temperatures and of water at 100°C. The shift of dν- 1050 with temperature and its highest intensity at 100°C are seen. In the spectrum of nitrate at 100°C the water band is more intense than even for pure water.

2. Sulphuric acid : Raman spectrum of 100% sulphuric acid consists of four groups of lines $d\nu = 380, 490, 910$ and 1150 and 1365 forming the fourth group comparing the spectrum with that of CCl_4. In addition, we have a line at 980 and a faint band at 3000 which corresponds to OH band. $d\nu = 980$ disappears on heating the acid to 350°C or on adding a small amount of water—it is absent in 98% acid. Lines 380 and 490 are highly depolarised and 910 is highly polarised similar to the $d\nu$ 459 of CCl_4, suggesting that it is of A_1 type and total symmetric. It is found to shift from 910 at 30°C to 890 at 350°C, as seen from the microphotometric records in Fig. I. As, normally, separation of molecules takes place at higher temperature, this reduction in frequency is quite unexpected.

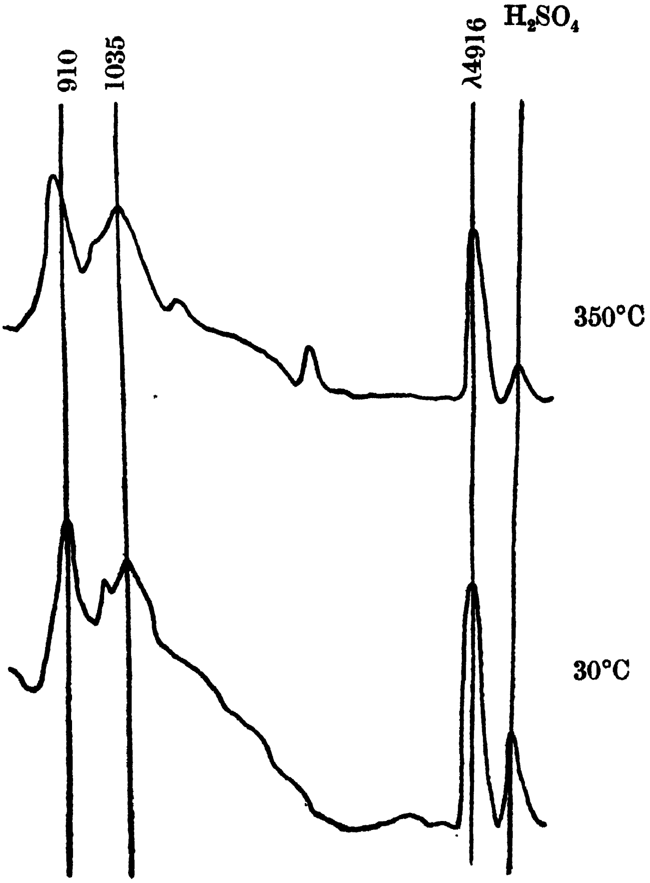

Fig. 1. Sulphuric acid at two temperatures. The shify of $d\nu = 910$ to lower frequency at higher temperature is seen.

3. Solution of Sodium nitrate : We wonder if we are dealing with molecules that are deformed during the formation of a complex. If this view is correct, we now cite a case where this is shown directly. Plate V shows Raman spectra of 5N sodium nitrate at 16°C, 40°C and 100°C and pure water at 100°C. The first spectrum is taken separately and others with a Hartman diaphragm.

NO_3, being of D_{3h} symmetry, is well known to show three Raman lines at $d\nu$ 720, 1050, 1390. But, the spectrum at 16°C contains a faint line at 594 in addition, making one suspect whether the ion has become pyramidal on hydration. If so, using the formula, given by Herzberg,

$$\cos^2\beta \qquad 1$$

$$\frac{4\nu^2_3\,\nu^2_4}{\nu^2_1\,\nu^2_2}+\frac{3m_y-m_x}{3m_y+m_x}$$

where, ν_1, ν_2, ν_3, ν_4, are respectively 1050, 594, 720, and 1390. m_y and m_x are masses of oxygen and nitrogen respectively, $\beta = 72° \ 12'$ for the angle between the axis of the pyramid and one of the NO bonds. This view is further supported by the fact that the total symmetric line 1050 shifts to lower frequency by 10 cm^{-1} on increasing the temperature from 16°C to 40°C and by 5 cm^{-1} for an increase from 40°C to 100°C.

A strong evidence for hydration is shown by the fact that this line increases both in intensity and width on heating. This is clearly demonstrated by the fact that λ4916 is of the same intensity at the two temperatures 40°C and 100°C while $d\nu$ = 1050 is much brighter at 100°C. This is in accordance with the evidence shown earlier to the effect that the bond stretching line decreases in intensity on forming a complex.

Another point of interest is the large increase in the width of the line $d\nu$ = 1050. If the width of the line is due to inter-ionic Stark Effect, widening of the line at higher temperature may be due to (1) decrease in the dielectric constant at high temperature and (2) closer approach of the ions of opposite sign. According to the model of a solution proposed by S. Lengyel, ions in a solution are completely surrounded by molecules of water, the first shell by strong and regular hydrogen bonds and others by comparatively randomly oriented molecules of water, keeping the ions of opposite sign well separated. On increasing the temperature, however, the hydration shell breaks down, permitting the ions to come closer. This is, perhaps, the first direct spectroscopic evidence for the formation of crystalline hydrates of ions in solution.

Another consequence of hydration is its effect on the determination of the degree of dissociation of acids by applying Raman Effect first introduced by Rao (1930), and followed by a number of others. In this method, the intensity of the line $d\nu$ = 1050 is measured in the spectra of nitric acid of various concentrations and assuming that it is proportional to the number of ions formed, the degree of dissociation is calculated. Now, if hydration is having some influence on the line, it introduces a large error in the determination of the degree of dissociation of the acid, especially at high concentrations as the amount of water available may not be sufficient to completely surround all the ions at all the concentrations.

Plate V shows another feature. Water band is stronger in the salt solution at 100°C than in the spectra on either side. It is well known that water band is very wide and it is due to hydrogen bonded clusters. As the water is heated, the band becomes narrower due to the clusters breaking down. It is also known that on adding a salt or acid, again the band becomes narrow. Now, while the width of the band does not change from 40°C to 100°C of the salt solution, it is much stronger at 100°C, showing that while the structure breaks down completely even at 40°C in the salt solution the ions which are surrounded by water forming hydrogen bonds are not relieved from this bondage. The molecules in salt solution at 100°C are free compared to those in pure water at this temperature.

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