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CHANGE IN THE SHAPE OF THF NO_3 ION DURING THE FORMATION OF A HYDRATE IN AQUEOUS SOLUTIONS

N. RAJESWARA RAO, K. V RAMANAIAH AND S. MOHANA RAO.

PHYSICS DEPARTMENT, OSMANIA UNIVERSITY, HYDERABAD

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It was reported by Rajeswara Rao and Ramanaiah (1964) that in a solution of sodium nitrate, the nitrate ion becomes pyramidal in shape at about 16°C and on heating to about 90°C it becomes planar. This conclusion was drawn to explain (1) a slight increase in the frequency of the total symmetric line $d\nu$ 1050 cm^{-1} at lower temperature where the ions can be expected to be hydrated better than at higher temperature and (2) appearance of a faint line at $d\nu = 594$ cm^{-1} which disappears at higher temperatures. The formation of the hydrogen bonding is evidenced by the low intensity of this line ($d\nu$ - 1050 cm^{-1}) at lower temperature.

During the formation of hydrogen bond, one normally expects the bond strength of NO to decrease. Increased frequency of the total symmetric line, however, throws doubt on this point. A normal coordinate treatment of pyramidal NO_3 ion is made and the force constants determined to settle this point.

The F and G matrices of pyramidal molecules are given by Venkateswarlu (1956). The bond length d of NO is taken to be 1.299 A.U. (Venkateswarlu) and the bond angle α between the NO bonds is 111°32′ and the frequencies are taken to be 594, 720, 1050 and 1420 cm^{-1}. This data are taken from a paper by some of the present authors referred to earlier. If one neglects $f_{d\alpha}$ (calculation justifies such an assumption), the secular equation reduces to two quadratic equations that can be readily solved. The force constants thus obtained are f_d - 7.127, $f_{dd} = 0.230$, $d^2f_\alpha = 1.818$, $d^2f_{\alpha\alpha}$ 0.233 in units of 10^5 dynes/cm. Comparing with $f_d = 7.848$, $f_{dd} = 1.281$ and $d^2(f_\alpha - f_{\alpha\alpha})$ - 0.2335, reported by Venkateswarlu for planar NO_3 ion, f_d is found to be smaller as one expects during the formation of hydrogen bond. Therefore, though the total symmetric stretch line slightly shifts to higher frequency, on hydration, the bond strength really decreases.

REFERENCES

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