THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part III. Discussion of the Infra-red Data

BY D. KRISHNAMURTI, F.A.Sc.

(Memoir No. 119 from the Raman Research Institute, Bangalore-6)

Received August 27, 1959

1. INTRODUCTION

Comparatively few investigations on the infra-red spectra of the hydroxides appear to have been made and even these mainly concern themselves with the 3 μ region. In the present part we shall discuss the data available for LiOH, LiOH·H₂O, NaOH, Ca(OH)₂ and Mg(OH)₂. Duval and Lecomte (1941) had reported the infra-red spectra of LiOH, Ca(OH)₂, Mg(OH)₂ and Al(OH)₃ for the region 600-1600 cm⁻¹ which falls outside the range of even the first order combinations of most of the lattice frequencies of these substances. In many of the cases studied by them there appear strong maxima in the region of 880 cm⁻¹ and 1440 cm⁻¹ corresponding to the strong absorption maxima usually observed with the carbonates. In view of the meagreness of the data for the lattice frequencies active in the infra-red and also since it appears to us that the substances used by Duval and Lecomte in their study have been contaminated by the atmospheric carbon dioxide to form the carbonates, we do not propose to discuss their data.

2. THE INFRA-RED SPECTRA OF LiOH, LiOH·H₂O AND NaOH

(i) LiOH and LiOH·H₂O.—The infra-red absorption spectra of LiOH and LiOH·H₂O have been recorded by Jones (1954) in the 3 μ region using thin films of the substances, the frequencies of the absorption maxima of the OH vibrations being respectively 3678 and 3574 cm⁻¹. The internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion in these two cases belong respectively to the classes A₂u of D₄h and B₁ of C₂h and are in each case the only infra-red active internal mode theoretically possible and hence the respective maxima at 3678 and 3574 cm⁻¹ are to be identified with them. That the infra-red frequencies in these cases are only slightly different from the Raman active frequencies is indicative of weak coupling between the hydroxyls. The diminution of the hydroxyl frequency in LiOH·H₂O by about 100 cm⁻¹ is hence largely to be attributed
to the proximity of the water molecules to the hydroxyls. Two other maxima at 3000 cm.\(^{-1}\) and 1586 cm.\(^{-1}\) respectively due to the stretching and bending vibrations of the water molecules in LiOH.H\(_2\)O have also been reported by him, the diminution in their frequencies being due to causes already discussed.

An absorption maximum at 7195 cm.\(^{-1}\) has also been observed by Jones in LiOH and identified as the overtone of 3678 cm.\(^{-1}\) According to theory this overtone is forbidden in the infra-red and only the combination between the Raman active (3664 cm.\(^{-1}\)) and the infra-red active (3678 cm.\(^{-1}\)) vibrations is allowed in the infra-red. Anharmonicity can be expected to be the cause of the violation of the selection rules. The large difference (161 cm.\(^{-1}\)) between the anticipated value for the overtone and the observed value indicates the presence of considerable mechanical anharmonicity. However, further studies are required to elucidate this feature more fully.

(ii) Sodium hydroxide.—The infra-red absorption spectrum of NaOH in the form of thin films has been studied by Busing (1955) and a sharp maximum at 3637 cm.\(^{-1}\) is reported by him. This is to be identified with the theoretically expected infra-red active internal vibration of the hydroxyls antisymmetrically with respect to the centre of inversion and belonging to the class B\(_{1u}\) of D\(_{oh}\). The small difference of 5 cm.\(^{-1}\) between the Raman active and infra-red active hydroxyl frequencies indicates that the coupling between the hydroxyls is very weak.

3. THE INFRA-RED SPECTRA OF Ca (OH)\(_2\) AND Mg (OH)\(_2\)

Unlike the above cases, the infra-red spectra of Ca (OH)\(_2\) and Mg (OH)\(_2\) exhibit complex structures in the 3 \(\mu\) region and it was therefore suspected that the actual unit cell of the structure should be larger than that derived from X-ray studies (Mara and Sutherland, 1953). However, reinvestigations of the structures by both X-ray and neutron diffraction methods have only revealed the correctness of the structure proposed earlier. So far, only tentative explanations have been offered for the complex features of the spectra.

It has already been shown in Table IV of Part II that in the cases of Ca (OH)\(_2\) and Mg (OH)\(_2\), there are possible four infra-red active fundamentals of which one is due to the internal vibrations of the hydroxyls antisymmetrically with respect to the centre of inversion and three others are due to translatory and rotatory oscillations. Besides these, the selection rules for combinations and overtones indicate that the combinations between the Raman active fundamentals and the infra-red active fundamentals (viz., A\(_{1g}\times A\(_{2u}\);