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The O-H Raman Frequency in Inorganic Acids

THE band characteristic of the OH group has been recorded in the Raman spectra of many hydroxides and alcohols. It has not so far been observed, however, in the case of the stronger acids. Using the improved technique of complementary filters recently developed by Ananthakrishnan[1], and giving long exposures varying from six to twelve days, I have succeeded in obtaining spectra with sulphuric acid and crystals of iodic, selenious and telluric acids, in which the band is clearly seen in the 4046 A. excitation. Table 1 gives the frequency shifts. The value for boric acid is taken from Ananthakrishnan's paper[2].

TABLE 1.

Substance	Raman frequencies of the OH band (cm.$^{-1}$)		
	Beginning	Middle	End
H_2SO_4 (100%) liquid	2794	2985	3172
HIO_3 crystals	2834	2979	3125
H_2SeO_3 ,,	2973	3057	3141
H_6TeO_6 ,,	2985	3121	3257
H_3BO_3 ,,	—	3172, 3256	—

The following points may be noted: (1) The OH frequency in these acids is represented by a band which is weak, broad and diffuse as compared with the other vibration frequencies. (2) The OH group, which gives a sharp line at 3608 in potassium hydroxide and a broad band at about 3660 in ethyl and methyl alcohols, gives a much lower frequency in the inorganic acids. (3) There is a progressive fall in the characteristic frequency shift and a diminished intensity of the band with increasing strength of the acid. (4) In the case of sulphuric acid, the band appears to be resolved into two components.

The fact that the OH band has not hitherto been recorded in the Raman spectra of acids has been regarded by some investigators[3] as supporting the hypothesis of the existence of the so-called hydrogen bond[4] in oxy-acids and their salts. Now that the OH band has actually been recorded, this view evidently requires some modification. We have in fact to postulate the existence of the OH bond in acids as well, but considerably weakened as compared with the strength of the bond in alkalis and in weak acids. It may be mentioned in this connexion that Badger and Bauer[5] have recently observed an infrared absorption band in the region of 3μ in sulphuric acid, and they ascribe it to the presence of the OH group. These authors have drawn the inference that the so-called hydrogen bond and the hydroxyl bond postulated by Bernal and Megaw[6] are only extreme cases of one and the same phenomenon. This view appears to be supported by the investigation reported above.

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