THE EFFECTS OF SULFURIC ACID AND OF ZINC CHLORIDE ON THE MAIN RAMAN BAND OF WATER

Sir:

In the course of a systematic study of the effects of dissolved salts, acids, and bases on the Raman spectrum of water, we have found that sulfuric acid and zinc chloride produce unique changes in the shape and in the frequency of the maximum of the main band, which are illustrated in the accompanying figures. The shift in the maximum is related to the concentration as follows, at 40°.

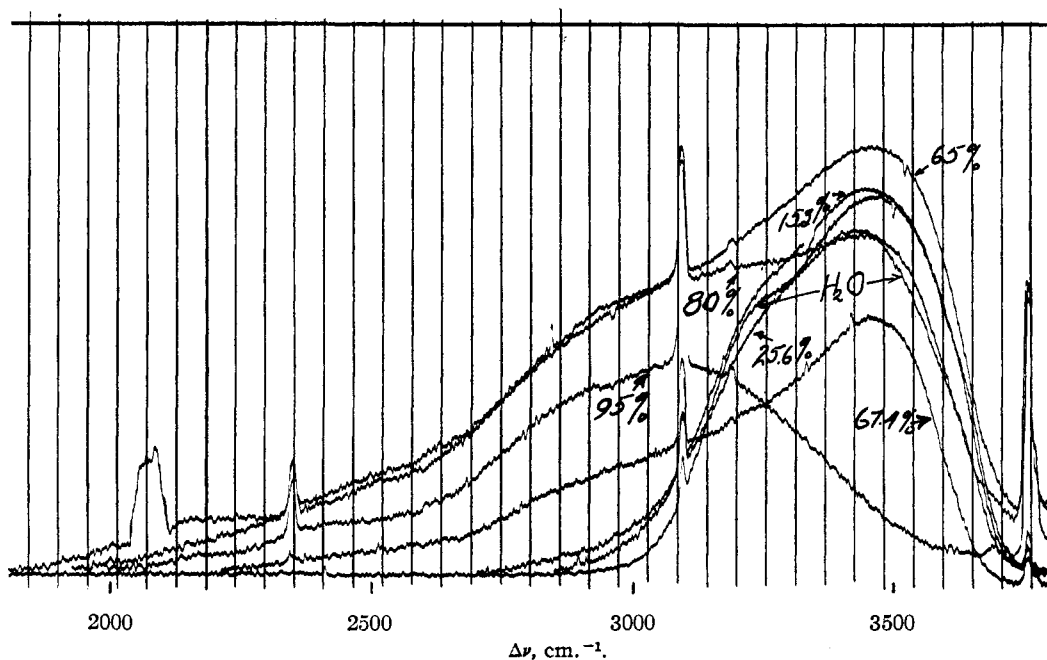| H_2SO_4, % by wt.	$\Delta\Delta\nu$, cm.$^{-1}$	$ZnCl_2$, % by wt.	$\Delta\Delta\nu$, cm.$^{-1}$
0.0	0	0.0	0
15.3	+ 14	14.3	+ 9
25.6	+ 34	31.6	+58
65.0	+ 32	41.8	+78
80.0	+ 20	50.0	+91
95.0	−336	57.1	+82

Fig. 1.—Showing the effect of various concentrations of sulfuric acid on the main Raman band of water.
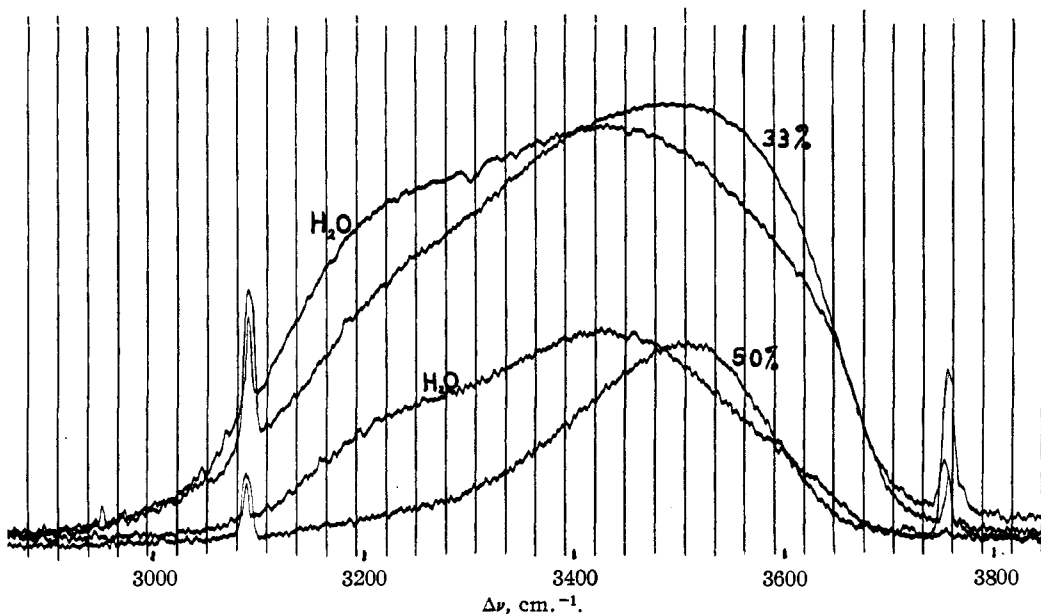

Fig. 2.—Showing the effect of 33% and 50% zinc chloride on the main Raman band of water.

The apparent broadening of the water band toward lower frequencies in sulfuric acid solutions of medium concentration (Fig. 1) is shown by the spectrum of 95% sulfuric acid to be due to the appearance of a new band, almost symmetrical in shape and with maximum at 3094 cm.$^{-1}$. A band at this frequency in pure sulfuric acid can only arise from a hydrogen or O–H vibration. Its width shows definitely that sulfuric acid is associated in the same manner as water and its change in intensity with dilution should be a function of the degree of ionization of sulfuric acid. In spite of the broadening toward lower frequencies, at concentrations below 65% the shift of the maximum toward higher frequencies in sulfuric acid is much larger than that in corresponding concentrations of sodium sulfate.

Like the alkaline earth chlorides, addition of zinc chloride to water causes the short frequency [ν(H)] component of the main band to disappear, indicating a dis-association of the solvent. While the net effect of this disappearance with the former compounds is to make the whole band more symmetrical, zinc chloride increases the asymmetry of the band and produces some three times as great a shift of the maximum as do alkaline earth chlorides in corresponding concentrations. The shift, which probably arises from and is an indication of the strong hydration of the zinc ion, increases up to a concentration corresponding approximately to one Zn^{++} to seven molecules of H_2O, it decreases with increasing concentration beyond that point.

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INHIBITORY EFFECT OF PACKING ON THE METHYL ETHER DECOMPOSITION

Sir:

In their work on the kinetics of methyl ether decomposition, Hinshelwood and Askey [*Proc. Roy.*

Soc. (London), **A115,** 215 (1927)] found that the rate in a silica bulb half-filled with powdered silica was appreciably lower than in a completely empty bulb. Thus at about 535° and 175 mm. initial pressure the values of t_{50} were 6.2 and 5.4 minutes for half-filled and empty bulbs, respectively. The packing thus decreased the rate by about 14%.

This effect, if real, is in harmony with the conclusion of Rice and Herzfeld [THIS JOURNAL, **56,** 284 (1934)] that the methyl ether decomposition involves long chains, the inference being that the chains may be broken at a silica surface by catalytic re-combination of the carriers. In order to obtain confirmation of the result, the following experiment was carried out.

Two Pyrex tubes, one empty and the other filled with 5 mm. Pyrex chips coated with potassium chloride, were bound together in a copper jacket and placed in an electric heater. Methyl ether vapor was introduced simultaneously into the two bulbs, and pressure differences and total pressures were determined.

The rate of pressure increase was definitely lower in the packed tube. In an experiment at 481°, the initial pressures were 458 and 440 mm. in packed and empty tubes, respectively. After twenty minutes, the corresponding pressures were 617 and 610 mm., giving increases of 159 and 170 mm. Correcting the latter for the lower initial pressure and for a small expansion (0.5%) gives 180 mm. for the corresponding pressure increase. The packing thus decreased the rate of pressure increase by 11.5%, as compared with the 14% reported by Hinshelwood and Askey.

It would seem to be clear that the reaction is not the simple homogeneous process originally postulated by Hinshelwood and Askey.

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