

Infrared Absorption Studies IV. The Infrared Spectrum of Water in an Inert Solvent

L. B. Borst, A. M. Buswell, and W. H. Rodebush

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the latter spectrum are well known and the vapor phase spectrum has been exhaustively investigated. If, therefore, the assumption that closely corresponding electronic transitions are involved in the excitation of all the molecules having the $-C-CH=CH-C-$ grouping is valid the absorption spectrum of benzene in the long wave region between 37,000 and 44,000 cm^{-1} would be ascribed to a singlet-triplet transition. Some justification for this assumption is given by the recent interpretation of the fluorescence spectrum of benzene by Ingold and Wilson¹⁴ in which a complete analysis of the spectrum was possible on the basis of transitions from three excited electron states to the zero level of the ground state.

¹⁴ C. K. Ingold and C. L. Wilson, J. Chem. Soc. 941 (1936).

The vapor pressure of the benzene was too high and the absorption tube too short to resolve the benzene spectrum sufficiently to permit detailed analysis of the bands but the general characteristics of the spectrum between 48,800 and 54,400 cm^{-1} and in the quartz region are sufficiently similar to indicate closely related electronic transitions. The probability of the singlet→triplet transition for ethylene was estimated by Mulliken to be of the order of 10^{-4} of that for the singlet→singlet transition and the ethylenic derivatives showed close agreement with that prediction. If the assumption of corresponding states for benzene is correct, comparison of the intensities in the two regions would show that the probability of the transition to the triplet state in benzene is about 10^{-2} of that for the singlet→singlet transition.

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Infrared Absorption Studies

IV. The Infrared Spectrum of Water in an Inert Solvent

L. B. BORST, A. M. BUSWELL AND W. H. RODEBUSH
University of Illinois, Urbana, Illinois

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The infrared absorption spectrum of H_2O , HDO and D_2O in dilute solution in carbon tetrachloride and carbon bisulfide has been investigated with a grating of high resolving power, in the region 2.6–3.8 μ . Several bands have been identified as ν_3 bands and the hitherto unobserved ν_1 band for H_2O is believed to have been found. The frequencies observed are compared with the same frequencies in the vapor and a displacement of frequency which is proportional to the frequency itself is observed in solution. A fine structure is observed in the case of H_2O which may be ascribed to rotation unless some other explanation is found. The spectrum in carbon bisulfide appears to be identical with that in carbon tetrachloride.

THE infrared vibration rotation spectrum of water vapor was investigated by Plyler and Sleator¹ and that of heavy water vapor has been recently studied by Barker and Sleator.² They have located the principal vibration frequencies for water and the two deuterium substituted molecules with the exception of ν_1 which has not been observed in the symmetrical molecule and ν_3 for HDO. ν_1 , however, has been observed

in the Raman spectrum for H_2O .³ Studies of hydrogen chloride absorption in solution have been made by Plyler and Williams,⁴ and West and Edwards.⁵ Recently Kinsey and Ellis⁶ have observed the infrared absorption spectrum of water in carbon bisulfide solution with a prism spectrograph.

³ D. Bender, Phys. Rev. **47**, 252 (1935).

⁴ E. K. Plyler and D. Williams, Phys. Rev. **49**, 215 (1936).

⁵ W. West and R. T. Edwards, J. Chem. Phys. **5**, 14 (1937).

⁶ E. L. Kinsey and J. W. Ellis, Phys. Rev. **51**, 1074 (1937).

¹ E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

² E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).

It seemed desirable to the authors to investigate the spectrum of water in an inert solvent with a spectrograph of high resolving power in order to determine what differences were produced in the spectrum by the presence of the

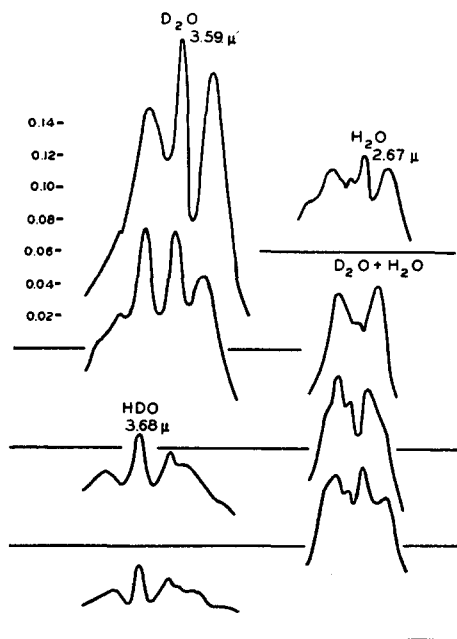


FIG. 1. Vapor absorption bands for mixtures of H_2O and D_2O . Prism spectrometer.

solvent molecules. A grating spectrograph which was purchased from the University of Michigan was available for this purpose. This instrument has been described.⁷ The grating was of the echelette type, 3600 lines to the inch, ruled on pure tin. It was constructed for us in the physics shop of the University of Michigan under the direction of Professor Barker. As a light source we used an ordinary street lighting bulb with a coiled tungsten filament of 6.6 amperes rating. The thin glass walls transmit very satisfactorily up to about 4μ and this type of lamp is much superior to the Nernst glower. The utmost precautions were taken in purifying the solvents used in preparing the solutions. As a check on the calibration of the grating, the absorption spectrum of vapor was recorded. The results agreed within about 3 cm^{-1} with those of Plyler and Sleator.

In measuring the absorption, a cell 7.5 cm in length with two compartments, one for pure

⁷ W. W. Sleator, *Astrophys. J.* **48**, 125 (1918).

solvent and one for solution, was used. When the absorption of the vapor was measured, the cells were heated by circulating water from a thermostat. In representing the data, wave numbers are plotted as abscissa and $\log I_0/I$ is plotted as ordinate, where I_0 is the galvanometer deflection through the pure solvent and I , the deflection when the solution is in the path.

The vapor absorption spectra of H_2O , HDO , and D_2O were mapped for comparison and identification purposes with a prism spectrometer of low resolving power (Fig. 1).

When a survey was made of the solution with the same instrument there was observed a band at 2.7μ due to H_2O and three bands between 3.5 and 3.8μ which were attributed to HDO and D_2O . These are shown in Fig. 2. The carbon

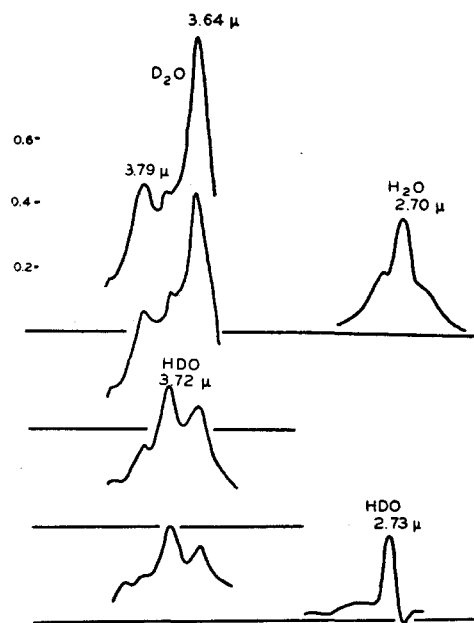


FIG. 2. Absorption bands of carbon tetrachloride saturated with a mixture of H_2O and D_2O . Prism spectrometer.

tetrachloride was saturated with water containing varying percentages of D_2O . It is evident that there is no very close correspondence between the absorption in the vapor and in solution. The main absorption peaks are undoubtedly due to the antisymmetric vibration ν_3 . It is suggested that the additional small peaks in solution, which have no counterpart in the vapor, might be due to the symmetric vibration

ν_1 which has not heretofore been observed in the infrared.

In Fig. 3 the absorption curves are given for H_2O in carbon tetrachloride solution as obtained with the grating spectrometer. The upper curve is obtained from a 12.5 cm layer saturated with water. (The solubility of water in carbon tetrachloride is stated to be 0.0083 mole per liter.) The lower curve is obtained by diluting the solution to one-fourth of the original concentration. The fine structure obtained here is believed to be real as it was checked repeatedly. In order to eliminate the possibility of water vapor in the system, the curves shown in Fig. 4 were obtained. The upper curve is the absorption curve for water vapor and the lower curve is for 5 cm

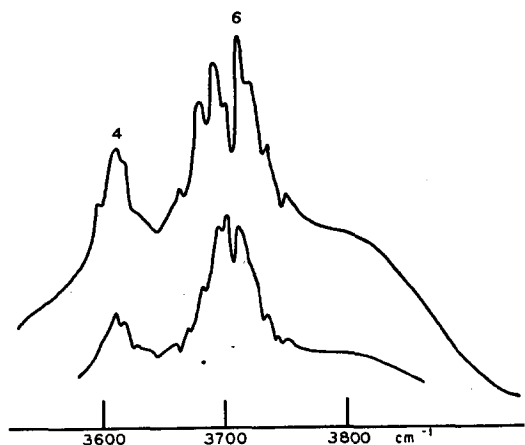


FIG. 3. H_2O in carbon tetrachloride. Grating spectrometer.

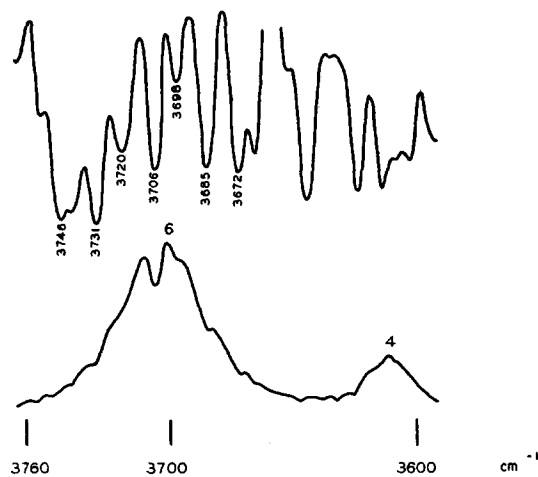


FIG. 4. Comparison of vapor and solution of H_2O . Grating spectrometer.

saturated carbon tetrachloride solution. There is no correlation observable.

Figure 5 is the absorption curve in the 2.7μ region for D_2O . The negative absorption simply indicates the presence of traces of water in the supposedly dry pure solvent. In spite of all precautions some water was present. In the cell to which D_2O was added this water was effectively converted to HDO . The peak is therefore to be attributed to ν_3 for HDO , the minima to the H_2O in the solvent. There is evidence of fine structure.

In Fig. 6 are given the absorption curves for three concentrations of D_2O in the region 3.4 to 3.9μ . The upper curve (dotted line) was obtained from a sample saturated with 99.6 percent D_2O . The middle curve was for a solution saturated with 85 percent D_2O and the lower curve was obtained upon diluting this solution one-half. The breaks in the lines are due to readjustment of the monochromator. These curves were obtained using the first order because of low intensity. The resolving power is therefore only one-half that used in obtaining the curves in Figs. 3, 4, and 5.

The identification of certain of the peaks seems obvious enough by comparison with the work of Sleator and colleagues. The frequency is shifted in solution to lower values, the shift being apparently roughly proportional to the frequency. Table I gives the principal absorption peaks. The number in the first column serves to locate the peak on the accompanying curves. The second column gives the frequency observed

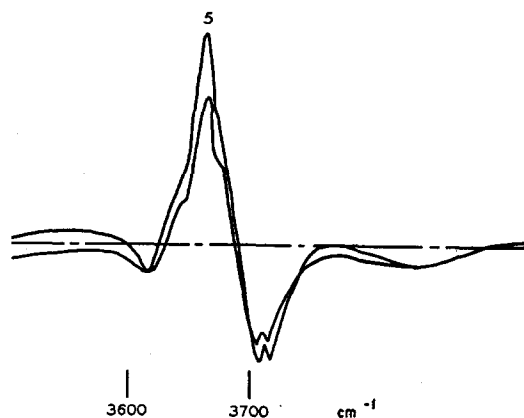


FIG. 5. Solution of D_2O in carbon tetrachloride. Grating spectrometer.

by us in carbon tetrachloride solution. The third column gives the frequency as observed in the vapor either by infrared absorption or in the

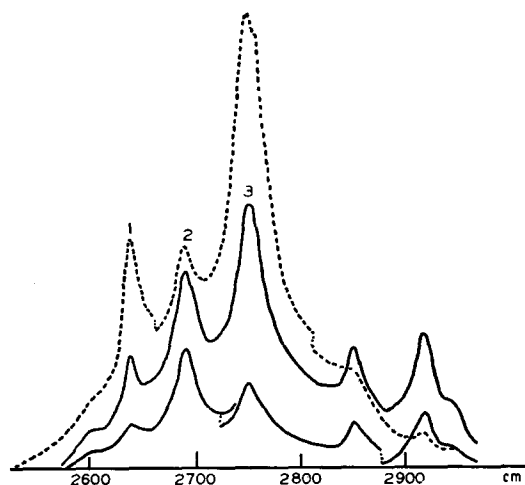


FIG. 6. Solution of D₂O in carbon tetrachloride. Grating spectrometer.

Raman spectrum. The fourth column gives the difference between solution and vapor. This difference is seen to be roughly proportional to the frequency and this can be justified on theoretical grounds. [ν_1] is enclosed in brackets since this frequency has not been observed before in the infrared and the assignment is therefore necessarily tentative since there is no very obvious reason why it should be more active in solution than in the vapor state. [ν_3] has not been observed for HDO either in the Raman or infrared spectra and the calculated value for the

TABLE I. Frequencies (cm^{-1}) of the principal absorption peaks.

	SOLUTION	VAPOR	DIFFERENCE
1	2640 [ν_1] D ₂ O	2666	26
2	2689 [ν_1] HDO	2720	33
3	2748 ν_3 D ₂ O	2784	36
4	3611 [ν_1] H ₂ O	3654	43
5	3659 [ν_3] HDO	[3750]	[91]
6	3702 ν_3 H ₂ O	3756	44

vapor [3750] may be in error by 50 wave numbers.

There seems to be no doubt as to the reality of the fine structure apparent in Fig. 3 and in the absence of other explanations it must be assumed to be due to some sort of submerged rotational structure. This fine structure was not observed in the deuterium substituted compounds for the reason that, assuming it to be a rotational structure, a higher resolving power would be required, whereas these spectra were observed in the first order with only half the resolving power used for ordinary water.

The absorption spectrum of water in solution in carbon bisulfide was observed but the curve is so nearly identical with those published here for the carbon tetrachloride solutions that there seems to be no reason for reproducing it.

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