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Vibrational-Rotational Radiation Transitions in Water Molecules In Nonpolar Solvents

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The $1.875\mu(\sigma+\delta)$ and $1.379\mu(\sigma+\pi)$ absorption bands of H_2O molecules in CCl_4 and CS_2 solutions and the $1.985\mu(\sigma+\pi)$ band of D_2O in CCl_4 are presented. They are interpreted as indicating free rotation of water vapor-like molecules in solution. The dominant feature of each band is an enhanced Q-branch. We are unable to decide to what extent this enhancement is caused by a possible departure from the usual rotational distribution characteristic of vapors and to what extent by possible alterations in transition probabilities.

We have previously shown[1] spectroscopically that there is free rotation of water vapor-like molecules when water is dissolved in carbon disulfide. This was demonstrated through a partial development in solution of rotational structure in the $1.379\mu(\sigma+\pi)$ and the $1.875\mu(\sigma+\delta)$ vibration-rotation bands. We found that there is a considerable alteration of relative intensities with respect to vapor band structure among the partially resolved rotational components, but we were not able to determine whether the branch whose intensity is enormously increased is a Q-branch or a P-branch. We have evidence indicating that it is a Q-branch.

This evidence was obtained in part by repeating our investigation with carbon tetrachloride as a solvent. This solvent was not tried before, because, as pointed out in our previous paper, data obtained from the *International Critical Tables* and elsewhere give the solubility of water in CS_2 as ten times greater than in CCl_4. This information is questionable, for the absorption bands obtained with saturated CCl_4 are more intense than with CS_2. If it is correct, then the transition probabilities for the bands differ greatly with the two solvents.

In this paper we are presenting the percentage transmission plots of the 1.379μ and 1.875μ bands of H_2O from vapor and from CS_2 and CCl_4 solution records, all determined under similar conditions of resolution in the recording spectrograph. The liquid water plots, which differ greatly from those of vapor and solution, are this time omitted. Also we are including the graph of the $1.985\mu(\sigma+\pi)$ band of D_2O, corresponding to the 1.379μ band of H_2O. The $(\sigma+\delta)$ band of D_2O is not obtainable with our spectrograph. A brief report[2] on H_2O in CCl_4 has already been made.

In Fig. 1 are plotted the 1.875μ vapor band and the corresponding bands of CS_2 and CCl_4 solutions. The slit width is indicated by the width of the line marked S. In a previous paper[1] we pointed out that Mecke's[3] partial analysis indicates that the central, most intense part of the vapor band is contributed to largely by Q-type transitions and hence we may refer to it as a Q-branch. And, although there is some overlapping of P, Q and R lines, the long and short wave-length portions of the band are essentially P- and R-branches. In the solution bands it appears fairly definite now that the Q-branch is greatly intensified and shifted to longer wave-length positions, the CS_2 shift being the greater. We are led to this conclusion primarily by the fact that, although in CS_2 the solution minima coincide in wave-length with certain vapor minima, in CCl_4 such a complete correlation does not occur. This interpretation finds further support in a comparison of the displacements of the water bands with those produced in other polar molecules by the same solvents. In Fig. 2 some of these displacements from the vapor positions are shown for comparison. Upward- and downward-pointing arrows indicate displacements in CCl_4 and CS_2 solution, respectively. In all instances the shifts are to longer wave-lengths, and wherever both solvents have been used the CS_2 displacement is the greater. The figure also shows

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[1] Kinsey and Ellis, Phys. Rev. **51**, 1074 (1937).

[2] Ellis and Kinsey, Phys. Rev. **53**, 672 (1938).

[3] Mecke, Zeits. f. Physik **81**, 313 (1933).

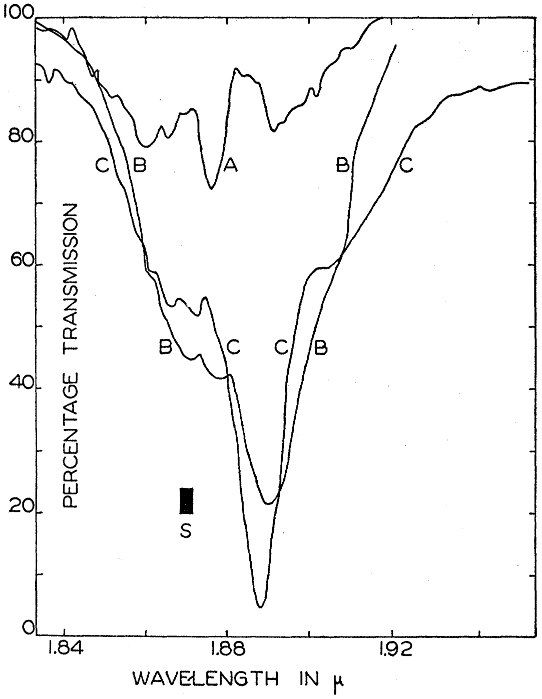

FIG. 1. The $1.875\mu(\sigma+\delta)$ H_2O band. *A*: Vapor. *B*: CS_2 solution. *C*: CCl_4 solution.

that in general frequencies which may be characterized as "OH frequencies" show greater shifts than "CH frequencies." Also the higher frequencies show greater displacements than the lower frequencies of the same type. The length of the horizontal double-headed arrow indicates the half-slit width in wave numbers, 5 cm^{-1}, corresponding to 0.2 mm on the record plate. A shift of this amount can be observed easily by the superposition of two transparent records.

In the solution bands of Fig. 1, structure is developed on both the high and low frequency sides of what we may now call the *Q*-branch. It is impossible, however, to correlate the structure satisfactorily with details of the vapor bands. This is not surprising because the *P*, *Q* and *R* lines overlap some and the resolution of the instrument is not complete. The failure definitely to establish a long wave shoulder in the CS_2 solution, corresponding to the one in CCl_4, can probably be explained by the presence there of a solvent band of nearly 100 percent absorption.

All of the solution bands of Figs. 1 and 3 were obtained with a 96 cm cell. The solution bands represent differential absorptions between saturated and unsaturated solutions. The unsaturated solutions were Eastman "highest purity" CCl_4 showing considerable residual water and Eimer and Amend CS_2 showing a trace of water after distillation over phosphorus pentoxide. The saturated solutions were obtained by shaking the specimens mechanically for several hours and allowing them to remain for several days before using.

In Fig. 3 are plotted the 1.379μ vapor band and the corresponding solution bands. From the similarity of appearances between this band and the 1.875μ one we again identify the strong component in the solution bands as a *Q*-branch. Although Mecke has recorded no *Q* line identifications, Dennison's[4] analysis of a perpendicular-type band indicates a central grouping of *Q* lines. The development of a short wave portion of the solution bands and the nondevelopment of the long wave portion is consistent with the great discrepancy in intensities in the two sides of the vapor band. As pointed out previously,[1] the absorption maximum at 1.468μ is to be interpreted not as a portion of the 1.379μ band but as a separate band $(\sigma+2\delta)$.

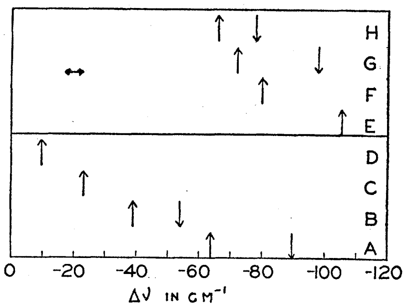

FIG. 2. Wave number displacements from vapor positions. *A–D*: CH bands. *E–H*: OH bands. *A*: Chloroform, 1.145μ. *B*: Chloroform, 1.680μ. *C*: Ethyl alcohol, 1.730μ. *D*: Formic acid, 1.727μ. *E*: Formic acid, 1.435μ. *F*: Ethyl alcohol, 1.395μ. *G*: Water vapor, 1.379μ. *H*: Water vapor, 1.875μ.

Figure 4 shows the $1.985\mu(\sigma+\pi)$ band of D_2O in CCl_4. An excess of 99.9 percent D_2O was shaken for $1\frac{1}{2}$ hours with 1 liter of CCl_4. The CCl_4 had been distilled over calcium chloride but still showed the presence of a considerable amount of H_2O. That there was no appreciable reaction

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[4] Dennison, Rev. Mod. Phys. 3, 280 (1931).

between the H_2O and D_2O to form HDO during the 3 hours required for mixing and obtaining the record was revealed by the intensity of the original H_2O band, which remained constant, and the absence of new strong bands. The D_2O band of Fig. 4 shows the general characteristics of the H_2O band of Fig. 3.

Although the full interpretation and significance of the intensity changes shown in Figs. 1, 3 and 4 must await the application of instruments of greater resolving power, we nevertheless think it is safe to state that in solution there is an enormous enhancement of *Q* lines over *P* and *R* lines. An application[1] of a calculation by Debye[5] to the problem of water in nonpolar solvents leads us to assume that most of the water molecules in CCl_4 and CS_2 solutions are free to rotate. We are, however, unable to decide to what extent the intensity enhancement of the *Q*-branch is caused by a possible departure from the usual rotational distribution characteristic of vapors and to what extent by possible alterations in transition probabilities.

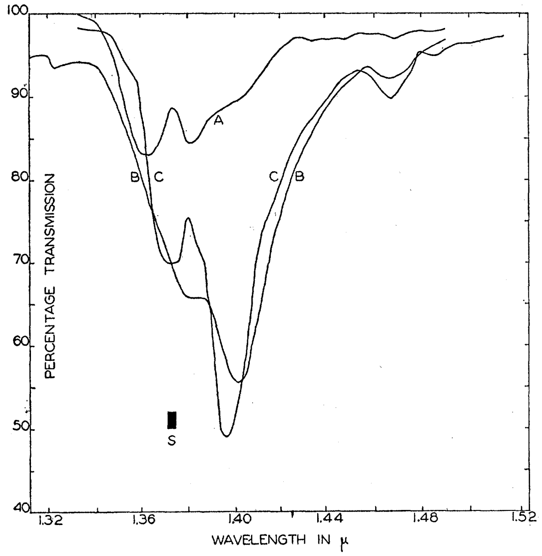

FIG. 3. The $1.379\mu(\sigma+\pi)$ H_2O band. *A*: Vapor. *B*: CS_2 solution. *C*: CCl_4 solution.

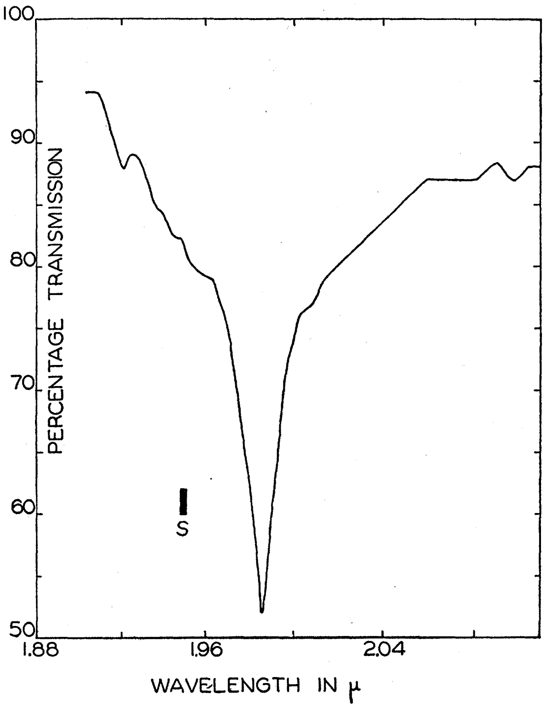

FIG. 4. The $1.985\mu(\sigma+\pi)$ band of D_2O in CCl_4.

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[5] Debye, Physik. Zeits. **35**, 100, 193 (1935).