ABSORPTION SPECTRUM OF WATER AT 300° IN THE RANGE FROM 4500 TO 1500 cm\(^{-1}\)

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Abstract

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ABSORPTION SPECTRUM OF WATER AT 300° IN THE RANGE FROM 4500 TO 1500 cm^{-1}

(Presented by Academician M. A. Styrikovich, 5 III 1970)

The study of changes in the vibrational spectrum of water when its temperature is raised by several hundred degrees has been carried out by a number of authors ($^{1-4}$). The most recent of these works were undertaken in order to establish which of the currently existing models of liquid water more fully satisfies the experimental data. Despite the thoroughness of the studies performed, it was not possible to obtain unambiguous conclusions (^{3,4}). One of the main reasons for this failure is the insufficient breadth of the spectral region studied. The latter is due to the fact that, because of the incompatibility of the requirements imposed on cuvette windows for the study of water at high temperatures (insolubility in water, high melting temperature, and good transparency), of the entire wide assortment of materials transparent in the infrared region of the spectrum, only sapphire was considered suitable ($^{2-4}$). Since the lower limit of sapphire transparency is at about 2150 cm^{-1}, cuvettes with such windows made it possible to study the temperature changes only of the bands of the fundamental stretching vibrations (^{2,3}) and their overtones (^{4}). However, measurements of spectra in this region proved insufficient for any definite conclusions about the structure of water in the liquid state ($^{4-6}$).

To extend the spectral region studied, in the present work pure single-crystal silicon, obtained by the zone-melting method and having a resistivity of 1500 ohm/cm, was used as the window material. Cylindrical windows 7.3 mm thick, sealed with Teflon rings, were separated by a copper gasket 0.035 mm thick. The design of the cuvette used was analogous to the design proposed by Fishman (^{7}) and additionally contained only a pressure sensor. The latter consisted of a Sylphon and a sample manometer, connected by a capillary tube and filled with Vaseline oil.* The diameter of the light beam passing through the cuvette was 5 mm. The absorption spectra were recorded with an IR spectrophotometer UR-20.

When a cuvette of this design is used, a significant fraction, relative to the light transmitted through it, is the intrinsic thermal radiation of the cuvette body

Fig. 1. Absorption spectra of a water layer 0.035 mm thick (solid lines) and 0.002–0.003 mm thick (dashed lines)

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and windows. At temperatures of 200, 250, and 300°, at a frequency of 1700 cm^{-1}, this ratio is respectively 0.28, 0.55, and 1.22. No less significant is the change in the transmittance coefficient of silicon in the frequency interval from 2500 to 1500 cm^{-1}, which at 300° decreases in comparison with its value at room temperature by a factor of 1.3–1.6. It follows from this that even approximate measurements of absorption spectra of heated samples in cuvettes with silicon windows require allowance for these corrections.

[*] The design scheme of the pressure sensor used was proposed by D. S. Tsiklis during discussion of the cuvette design, for which the authors express their sincere gratitude to him.

On a standard spectrophotometer in which the modulator is located after the cuvette compartment, measurements of the spectra of heated substances in cuvettes with low-transparency windows can be carried out in the following way. In a purely formal manner, certain fictitious transmission coefficients are recorded for the cuvette with the sample, $I^*_{\text{co}}(\nu)$, and for the cuvette without the sample, $I^*_{\text{c}}(\nu)$, and then also for the cuvette with the sample, $I^{**}_{\text{co}}(\nu)$, and for the cuvette without the sample, $I^{**}_{\text{c}}(\nu)$, but now with the light beam blocked before the cuvette compartment.

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Obviously, in this case the instrument-recorded quantities $I^{**}_{\text{c}}(\nu)$ and $I^{**}_{\text{co}}(\nu)$ will be equal to the emissive powers of the cuvette $\Phi_{\text{c}}(\nu)$ and of the cuvette with the sample $\Phi_{\text{co}}(\nu)$, referred to the radiation of the light source at the same wavelength. In this notation,

$$I^*_{\text{c}}(\nu) = I_{\text{c}}(\nu) + \Phi_{\text{c}}(\nu),$$

and

$$I^*_{\text{co}}(\nu) = I_{\text{co}}(\nu) + \Phi_{\text{co}}(\nu),$$

where $I_{\text{c}}(\nu)$ and $I_{\text{co}}(\nu)$ are the desired true transmission coefficients of the empty cuvette and of the cuvette with the sample, respectively. If the measured spectra are then recalculated by the formula

$$\frac{I^*_{\text{co}}(\nu) - I^{**}_{\text{co}}(\nu)}{I^*_{\text{c}}(\nu) - I^{**}_{\text{c}}(\nu)},$$

we obtain the true value of the transmission coefficient of the sample itself.

Application of the indicated method of measurement and processing of the results made it possible to obtain the absorption spectrum of a water layer 0.035 mm thick in the region from 4500 to 1500 cm^{-1}, at the pressure of saturated vapor, up to a temperature of 300°. As a result, for the first time it proved possible to observe the influence of temperature on the band of the fundamental deformation vibration of the water molecule and on the combination band of deformation and librational vibrations (Fig. 1). The spectra of a 2–3-micron layer of water situated between two sapphire windows are also presented here.

As can be seen from the figure, the temperature changes of the combination band at 2150 cm^{-1} are quite different from the temperature behavior of the previously studied bands of the fundamental stretching vibrations of water and their overtones. This 2150 cm^{-1} band differs from the former bands in the direction of the temperature shift, and from the overtones both in the direction of the shift and in the opposite behavior of the intensity change. At the same time, both for the bands of the fundamental stretching vibrations and their overtones, and for the 2150 cm^{-1} band, the monotonic character of all its temperature dependences is clearly observed, without even any hint of discontinuity. The deformation-vibration band, within the accuracy of the measurements carried out, and in contrast to all the other bands studied, does not depend on temperature. The behavior observed by us for the complex band of stretching OH vibrations

···completely agrees with the results of her earlier studies ([2,3]).

The authors consider it their pleasant duty to express their sincere gratitude to M. A. Styrikovich for proposing the problem, for discussion, and for his constant interest in the work, and also to M. S. Churakov for assistance in carrying out the experiment.

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