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Abstract

Full Text

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V. M. ZOLOTAREV

APPLICATION OF THE METHOD OF FRUSTRATED TOTAL INTERNAL REFLECTION TO THE MEASUREMENT OF ABSORPTION AND DISPERSION OF LIQUID WATER IN THE REGION OF THE STRETCHING-VIBRATION BAND

(Presented by Academician A. N. Terenin, 31 XII 1965)

The study of the optical constants of water was begun in 1892 by Rubens, who measured the dispersion of water in the near infrared region of the spectrum. Up to the present time, the vibrational spectrum of water has been the object of intensive investigations by means of a wide variety of methods. The most promising of the available methods for studying the vibrational spectra of water are the methods of infrared spectroscopy and combination scattering (Raman scattering). However, the application of these methods to the determination of quantitative characteristics of aqueous systems encounters considerable difficulties specific to each of the methods. In particular, the use of the classical methods of infrared absorption and reflection spectroscopy meets serious methodological difficulties when working in the range of values of the absorption index $k \geq 0.02$. The use of the method of normal-incidence reflection, because of its low sensitivity when working in the range of values of the absorption index $0.002 < k < 0.4$ (characteristic of aqueous systems), does not make it possible to obtain complete information about the structure of the water band, although it does make it possible to determine the spectral behavior of the optical constants n and k ($\bar{n} = n - ik$) (^{1}).

At present there are many contradictory data on the optical constants of water (^{2}-^{4}), the use of which for calculating various characteristics (absorption, reflection, emissivity, etc.) may lead to incorrect results. The data most consistent with one another for the extreme values of n and k of water are given in works (^{1}, ^{3}), in one of which a single maximum was found in the absorption, whereas according to the available data (^{5}-^{13}) the stretching band of water has a more complex structure. In this connection we attempted to find the values of the optical constants n and k in the region of the stretching-vibration band of water by a new independent method. The most suitable for this purpose, as follows from comparison of the results of a number of works, is the method of frustrated total internal reflection (F.T.I.R.) (^{1}, ^{14}, ^{15}), which was the method used by us.

The measurements were carried out with the aid of an SP-122 attachment (^{16}) on a Hilger H-800 instrument; the accuracy of measuring the reflection coefficient $R \leq 0.5\%$. In the attachment a prism of oxygen-free glass with a radius of 30 mm was used. For greater reliability of the initial data, measurements were made twice for each of three angles of incidence: 35, 40, and 45°. The choice of the polarization state of the incident radiation for each of the angles of incidence was made with allowance for the optimum accuracy in determining n and k (^{14}, ^{15}). The calculations of n and k were carried out from tables compiled with the aid of the "Ural" electronic computer. The error in determining n and k on the long-wavelength wing of the band is 0.5 and 5%, respectively; on the short-wavelength wing the accuracy was substantially lower and was approximately 5 and 25% for n and k. The results obtained are presented in Fig. 1.

As is seen from the figure, the absorption band of the valence vibrations of liquid water is complex and consists of three strong bands with maxima at 3320, 3420, 3490 cm^{-1}, as well as a weaker band at 3600 cm^{-1} (and, possibly, at 3200 cm^{-1}).

Table 1

(^{5})	(^{6})	(^{7})	(^{8})	(^{9})	Our data	(^{9})	(^{10})	(^{11})	(^{12})	(^{13})
3200	3280	3280	3290	3290	( )3200	3250	3050	3224	3200	3260
3400	3400	3400	3450	3425	3320	3430	3210	3436	3435	3426
				3480	3420	3480	3450			
3600					3490		3610	3625	3600	3610
					3620					
i.-r.	i.-r.	i.-r.	i.-r.	i.-r.	i.-r.	Raman	Raman	Raman	Raman	Raman

For comparison, Table 1 gives the frequencies of the maxima in the band of the valence vibrations of liquid water according to data from various authors. The best agreement of the results obtained by us is observed with the data of work (^{9}), in which the measurements were carried out by two independent methods. Experimental difficulties apparently complicated the clear separation of the bands at 3420 and 3490 cm^{-1} in works (^{7,8}), although in the spectra presented in work (^{7}) one can find indications of the presence of a band at 3500 cm^{-1} and even at 3600 cm^{-1}. As can be seen from the data of works (^{9,10}), in the Raman spectra of liquid water, in contrast to the data obtained by the method of infrared absorption spectroscopy, the intensity of vibrations in the region of 3100 and 3600 cm^{-1} increases, which leads to a strong broadening of

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Fig. 1. Optical constants of liquid water

Figure 1: Fig. 1. Optical constants of liquid water

the band and makes it difficult to distinguish individual maxima. In our case, as it seems to us, the course of the refractive index in the region of the band is to some extent a criterion for the correct identification of strong maxima.

Fig. 1. Optical constants of liquid water.

The extreme values of the optical constants obtained, both in position and in their absolute value, agree fairly well with the results obtained in works (1,7); the data on the integral intensity ($4.6 \cdot 10^{-6}$ cm^{-2}) and the half-width (370 cm^{-1}) of the investigated band are also in good agreement.

In general, from consideration of the materials obtained and their comparison with literature data, one may conclude that the method of frustrated total internal reflection is very promising for obtaining quantitative data on the absorption and dispersion of aqueous systems, possessing, in comparison with existing methods, more high-

with high accuracy and resolution. It may be assumed that the application of this method, along with others, will make it possible to refine the assignment of the maxima of the valence band of liquid water to individual molecular vibrations.

In conclusion I express my deep gratitude to N. G. Bakhshiev for discussion of the results obtained and to B. S. Neporent for his attention to the present work.

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