INFRARED SPECTRUM OF WATER AND AQUEOUS SOLUTIONS OF ACETONITRILE IN THE REGION OF LIBRATIONAL VIBRATIONS OF THE WATER MOLECULE

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Abstract

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INFRARED SPECTRUM OF WATER AND AQUEOUS SOLUTIONS OF ACETONITRILE IN THE REGION OF LIBRATIONAL VIBRATIONS OF THE WATER MOLECULE

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The broad band with a maximum near 700 cm^{-1} in the infrared spectrum of liquid water is usually attributed to rotational librations of water molecules bound by hydrogen bonds to their neighbors (^{1,3}). There is no convincing, generally accepted interpretation of the details of this spectral region (^{2}). This same band in the combination-scattering spectrum of water is treated by most investigators ($^{3-7}$) as a superposition of three bands corresponding to the three principal moments of inertia of the water molecule. Recently Walrafen (^{7}) did indeed distinguish in it three bands with maxima at 420, 530, and 720 cm^{-1}. Since in the infrared spectrum the vibration of the water molecule about the second-order symmetry axis is inactive, the infrared librational band should accordingly consist of only two bands with maxima at 550 and 720–740 cm^{-1} (^{3,7}).

In the present work a new, structural interpretation is proposed for the librational spectrum of water and sufficiently dilute solutions of acetonitrile in water. A first attempt at a structural interpretation of the infrared librational band of water was undertaken by us in papers (^{2,8}), where it was established that, both in pure water and in aqueous acetonitrile solutions of any concentration, the band is asymmetric and that, with increasing acetonitrile concentration beginning at 16 mole %, its principal maximum gradually shifts toward lower frequencies. Two typical experimental contours of the band are shown in Fig. 1.

It turned out that the shape of the high-frequency edge of the band is very well described by a Gaussian function

$$D(\nu) = \exp\left[(\nu - \nu_0)/\sigma\right]^2 .$$

Here $D(\nu)$ is the optical density at frequency ν, normalized to unity at the prin-

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

cipal maximum; ν_0 is the frequency of the principal maximum; σ characterizes the width of the band.

The frequency dependence of the excess intensity in the low-frequency part of the band is shown in Fig. 2. The zero background is subtracted in such a way that at 300 cm^{-1} the excess intensity proves to be vanishingly small in comparison with the intensity of the principal Gaussian component. Analysis of Fig. 2 shows that the excess intensity can also be resolved into two approximately Gaussian bands, both in pure water and in solution.

Table 1 gives the quantitative characteristics of all three bands of the infrared spectrum. Also indicated there are the fractions φ_i that each band contributes to the total intensity. The φ_i were calculated by the formula

$$\varphi_i = \sigma_i D_i \Bigg/ \sum_{i=1}^{3} \sigma_i D_i,$$

since the area under a Gaussian curve is proportional to σD.

First let us consider in more detail the case of pure water. The frequency of both weak peaks agrees well with the frequencies in the Raman spectrum of pure water obtained by Walrafen (^{7}). The very fact that there are three coincident bands in the IR spectrum and in the Raman spectrum already makes it possible to reject the interpretation proposed by Walrafen (^{7}), especially since the intensity of the 435 cm^{-1} band (corresponding to vibration about the symmetry axis of the second-order axis) in the IR spectrum proved to be much greater than that of the 525 cm^{-1} band. Apparently the point of view of Blue (^{9}), who believes that differences in moments of inertia cannot lead to strong splitting of the bands (by more than

Fig. 1. IR spectrum of pure water (*a*) and of an aqueous solution of acetonitrile (25 mol.%) (*b*). The dashed line shows the principal Gaussian component. The optical density at the band maximum is taken as unity.

Fig. 2. Difference between the observed intensity and the principal Gaussian component in the IR spectrum of pure water (*a*) and of an aqueous solution of acetonitrile (25 mol.%) (*b*).

10%), is close to reality. Evidently, for a correct explanation of the complex structure of the librational spectrum of water, structural concepts should be invoked, and each band should be regarded as corresponding to a definite structural type of water molecule.

At present, in describing the structure and properties of water and aqueous solutions of nonelectrolytes, the best results are given by the ice-like model of the structure of water due to O. Ya. Samoilov (^{10}, ^{11}), according to which water molecules form a framework, part of whose voids is filled. In this simplified model there are only two structural types of water molecules: tetrahedrally coordinated molecules and unbound interstitial (hydrophobic) molecules. But such a model is insufficient for explaining the librational spectrum.

Table 1

Band No.	Pure water	Pure water	Pure water	Pure water	Water—acetonitrile (3:1)	Water—acetonitrile (3:1)	Water—acetonitrile (3:1)	Water—acetonitrile (3:1)
	ν_0, cm^{-1}	σ, cm^{-1}	D	ϕ	ν_0, cm^{-1}	σ, cm^{-1}	D	ϕ
1	700	245	1.0	0.945	700	205	1.0	0.889
2	525	50	0.07	0.015	520	40	0.19	0.032
3	435	65	0.16	0.040	440	65	0.28	0.079

One of us has proposed another approach to the problem of the structure of water, which proceeds from recognition of the existence in water of an ice-like framework, but assumes the possibility of hydrogen-bond formation between interstitial and framework molecules (^{12}). This idea is supported by analysis of the radial distribution curve of water (^{13}). In addition, the temperature dependence of the coordination number and density

is explained if one assumes that the cavity molecules belong to two different classes [14]: hydrophobic molecules and molecules connected with the framework, “hydrophilic” molecules. Thus, in water there are three types of molecules: framework (80%), hydrophobic (4%), and hydrophilic (16%) cavity molecules (these figures refer to 30°). It seems very attractive to correlate with them the three bands in the librational spectrum. However, such an interpretation is incompatible with the librational spectrum of water in acetonitrile solutions (Fig. 2). There is no doubt that, at least in dilute solutions, the origin of the three bands must be the same as in the case of pure water. This is indicated above all by the coincidence of the component frequencies. But if the main component (700 cm^{-1}) is associated with rotational rocking of the framework molecules, then, while remaining within the ice-like model, it is difficult to understand its weakening down to complete disappearance as the concentration of acetonitrile increases, with a simultaneous strengthening of the bands of the cavity molecules [8].

It is very curious that the structure of the librational band can be understood by means of a model in which hydrophobic and hydrophilic molecules are spatially separated and form two structures [15]. One ice-like structure is an ice-like framework, an insignificant part of whose cavities is occupied only by hydrophobic molecules; the other—a disordered structure—is also an ice-like but strongly distorted framework, most of whose cavities are filled with hydrophilic molecules. A joint analysis of the coordination numbers, density, and compressibility of water leads to the conclusion that at 30° 55.5% of the molecules enter the disordered structure; of these, 72% build the framework and 28% are in cavities. In the cavities of the ice-like structure there are only 8% of the molecules forming it. With increasing temperature, the relative number of molecules of the disordered structure increases only slightly, whereas the fractions of hydrophilic and hydrophobic molecules in their structures increase more sharply.

From this point of view, the interpretation of the librational spectrum may be as follows: the main Gaussian component corresponds to framework molecules of the ice-like structure. The bands at 435 and 525 cm^{-1} are due, respectively, to framework and hydrophilic cavity molecules of the disordered structure. The number of hydrophobic molecules is small, and they do not appear* against the background of the principal band (700 cm^{-1}). That the peak at 435 cm^{-1} corresponds specifically to framework molecules follows from the fact that its intensity is higher than that of the 525 cm^{-1} band, not only in the IR spectrum but also in the Raman spectrum, whose intensity is more directly connected with the occupation numbers of the corresponding states [7]. It is interesting that the estimates of the intensities in the Raman spectrum [7]—50, 30, and 18%—are in general agreement with the concentrations of molecules of different types in the proposed interpretation of the two-structure model (40, 40, and 16% at 30°).

Having adopted the indicated interpretation of the spectrum, one can proceed to elucidate the structure of water in acetonitrile solutions. In doing so it is necessary to take into account that the intensity of the IR spectrum depends substantially on the change in the dipole moments of the molecules during vibrations. It is natural to suppose that in the ice-like structure, in contrast to the disordered one, there is a strong correlation of the directions of the dipole moments of large groups of molecules [16]. Apparently, it is precisely for this reason that, when the concentrations of framework molecules in the two structures are equal, their intensities differ by approximately a factor of 20. To take this circumstance into account, let us write $\varphi_i = \gamma_i n_i$ $(i = 1, 2, 3)$; n_i is the fraction of molecules giving rise to the band (the numbering of the bands is given in Table 1). Knowing the relative amounts of molecules of different types in pure water [15] and using the values—

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* If hydrophobic molecules rotate freely, the corresponding band in the librational spectrum should be absent altogether.

Table 2

	y	f_s	f_h	n_1	n_2	n_3	γ_2/γ_3	γ_1/γ_3
Water at 30° (15)	0.445	0.92	0.72	0.41	0.155	0.40	–	–
Water – acetonitrile (3 : 1)	0.27	1	0.70	0.27	0.22	0.51	0.93	21.2

Using the values of φ_i given in Table 1, one can calculate the ratios of the coefficients γ_i from the relations:

$$n_1 = yf_s, \qquad n_2 = (1-y)(1-f_h), \qquad n_3 = (1-y)f_h,$$

where y is the fraction of molecules (of the total number of water molecules) forming an ice-like structure; f_s and f_h are the fractions of framework molecules in the ice-like and disordered structures.

Assuming that in solution the γ_i retain the same values, one can obtain information about the change in the structure of water in acetonitrile solution from the experimental values of φ_i. For example, f_h and y can be found from the equations

$$\frac{f_h}{1-f_g} = \frac{\gamma_2}{\gamma_3}\frac{\varphi_3}{\varphi_2}, \qquad \frac{y}{1-y} = \frac{\gamma_3}{\gamma_1}\frac{\varphi_1}{\varphi_3}\frac{f_h}{f_s}.$$

The results of such calculations and the initial data for pure water are given in Table 2. Note that f_h is found accurately, whereas the estimate of y is based on the assumption* $f_s = 1$.

Thus, in solution both the total content of the disordered structure and the fraction of hydrophilic molecules in it increase. On the whole this confirms the suggestion, expressed in works (2, 8), that the structure of water is destroyed in an aqueous acetonitrile solution at concentrations above 16 mole %. We emphasize that this destruction is not so great that the model loses its meaning. Indeed, no fewer than 2/3 of the molecules may be in the ice-like framework. Thus, the interpretation described proves to be internally consistent. It agrees well with the interpretation based on the two-structure model of Raman spectra (7), both in the region of librational and in the region of stretching vibrations.

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* As is seen from Figs. 1 and 2, hydrophobic molecules also do not make a noticeable contribution to the librational IR spectrum in solution.

Note: Figure translations are in progress. See original paper for figures.