Raman spectra and *ab initio* calculation of a structure of aqueous solutions of methanol

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ABSTRACT

Small amount of low molecular weight alcohols leads to appearance of some special properties of alcohol-water solutions. In the literature it is associated with structural changes in solution with changing concentration. However, the problem special properties and structure of solutions at low concentration of alcohol is not very clear. Accordingly, we carried out quantum-chemical calculations and experimental studies of aqueous solutions of methyl alcohol.

The calculations performed for ten molecular alcohol-water mixtures showed that with a low concentration of methyl alcohol in water the solubility of alcohol is poor: the alcohol molecules are displaced from the water structure and should form a particular structure. Thus, with low concentration of alcohol in the aqueous solution there are two types of structures: the structure of water and the structure of alcohol that should lead to the presence of specific properties. At high concentration of alcohol the structure of water is destroyed and there is just the structure made of alcohol-water aggregates. This interpretation is consistent with the experimental data of Raman spectroscopy. The band of C–O vibrations of alcohol is detected to be of complex character just in the region of the presence of specific properties.

Formation of intermolecular H-bonds also complicates the Raman spectra of O–H or O-D vibrations of pure alcohol: a non-coincidence of peak frequencies, a shift of the band towards low-frequency region, a strong broadening of the band.

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1. Introduction

Low content of low molecular weight alcohols leads to the presence of specific properties of alcohol-water solutions. In the literature it is associated with a change in the structure of the solution with concentration. In 60–70 years of the last century it was found [1] that small additions of alcohols to water produce an additional narrow peak in the concentration dependence of the intensity of the Rayleigh light scattering. This effect was explained by structural changes in water with addition of alcohols and this maximum was called a structural one. At high concentrations of alcohol there is another broad maximum associated with the usual concentration fluctuations.

Concentration dependence of the position of the narrow peak varied depending on the number of alcohol, and the intensity of this peak changes with temperature. The mechanism of appearance of the maximum remained not very clear.

In Ref. [1] author gives the following explanation for the origin of the narrow peak. "While the alcohol concentration is low, its molecules are introduced into the lattice of water without destroying its structure. The introduction of the alcohol molecules need to be treated as follows: polar O–H groups displace water molecules from the lattice, and the more extensive hydrophobic atomic groups are included in the cross-site cavities." In this regard we need more facts to elucidate completely the mechanism of the appearance of this additional peak.

In Ref. [2] the absolute intensity of the line of Raman scattering was studied in methanol, ethanol and water in the gas and liquid phases. Big changes were observed in the intensity of the Raman lines of OH stretching vibrations in the transition from gas to liquid. The observed changes in intensity are interpreted as due to the

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additional contribution of charge transfer of electronic excited state arising from the formation of hydrogen bonds. To confirm weakening of the hydrogen bond with addition of methanol in water authors of [3] studied the Raman spectra of methanol in water solutions and show that the non-coincidence of maxima of the frequency of CO Raman band decreases with decrease of the concentration of methanol in the solution. This behavior can be explained as the effect of reducing the methanol-methanol hydrogen bond with the addition of water, which is attributed to the asymmetry of the band caused by the orientation dynamics.

Polarization and temperature study of Raman spectra [4] also showed that the spectral bandwidth is changed and, respectively, there is the change in the relaxation time with the change of the movement of molecules with hydrogen bonds.

Accordingly, we decided to carry out non-empirical (ab initio) calculations and experimental studies of vibrational spectra with the hope to clarify the mechanism of the appearance of the additional maximum in such calculations and experiment.

2. Calculations and experimental method

Raman spectra were recorded with the help of an automated spectrometer DFS-52, which is a double monochromator with two gratings of 1800 lines per mm. The excitation source was argon laser LGN-503 with the wavelength of 488 nm at the output power of 1 W. All measurements were performed at $90°$-scattering geometry in polarized excitation light and at the temperature of $20°C$. Quantum chemical calculations were carried out in the RHF approximation with a set of Gaussian functions $6\text{-}31G{+}{+}(d, p)$ [5].

3. Results and discussion

At normal room temperatures, there is no phase separation of low molecular weight alcohols in alcohol-water mixtures. This means that some interaction of alcohol molecules with water molecules occurs. In Refs. [6,7] all concentrations of the methanol-water solution were studied, and it was shown the non-coincidence of frequency of peaks in polarized components of the Raman spectra due to hydrogen bonding. We carried out ab initio calculations to determine the structure of methanol-water aggregates. A consistent analysis of experimental data is based on ab initio anharmonic calculations of the structure and vibrational spectrum of the complexes. In the first stage at a good level a potential surface of the complex is calculated ab initio, the geometry of the complex is determined and then the anharmonic vibrational problem is solved. Full optimization of the geometry of the molecule is a search for the minimum of the total energy according to of all the geometric parameters. In a molecule consisting of N atoms and not having symmetry, the number of parameters is $3N{-}6$ (3 N degrees of freedom minus translations and a rotation of the molecule, as a whole, around three axes). This number of independent parameters defines the dimension of the space in which the potential energy surface is constructed. To study the structure it is very important to find stationary points of the potential surface where the first derivatives of the energy become equal to zero. A type of the stationary point (minimum, maximum, saddle point) is determined by the second derivative. Diagonalization of the matrix of second derivatives gives the normal vibration frequencies, signs of which determine the type of the stationary point. If the frequencies of all normal vibrations are positive, then the singular point is the minimum. If one of the eigenvalues is negative, then we deal with the saddle point. In the process of optimizing the geometry the program produces analytical calculation of forces on the atoms (the first derivatives of the energy with respect to coordinates or gradient). The magnitude of the gradient determines the increment

of the corresponding coordinate, and its sign determines the direction. A set of gradients characterizes the direction (vector) of descent, according to which the program determines a new geometry of the molecule corresponding to a lower value of the total energy. Then the whole cycle of calculation is repeated for each new geometry until the forces on atoms and change of the geometric parameters and the total energy become close to zero. Quantum chemical calculations were performed using the Gaussian-03 software package in RHF approximation using a set of basis functions $6\text{-}31G{+}{+}(d,p)$ [5]. We attempted to determine the structure of the aggregates of water molecules. The calculations were performed for model aggregates (clusters), including from one to ten molecules of water and alcohol. Geometry of the model aggregates was obtained by probabilistic modeling with the subsequent ab initio optimization.

Calculations were performed for 10 units of alcohol and water molecules. First, the structure was determined for 10 water molecules [8]. After that we determined the structure of 9 water molecules and 1 molecule of alcohol, 8 molecules of water and 2 alcohol molecules, and so on, until the molecular structure of 10 alcohol molecules. Both water and alcohol are substances in which hydrogen intermolecular bonding plays a determining role. Both for water and alcohols a formation of multi-molecular aggregates is characteristic [8–10]. For methanol a band of the stretching O—H and O-D vibrations is presented in Fig. 1 and Fig. 2 in different polarizations of the scattered light. The figure shows that the bands of O—H and O-D vibration are complex, and they consist of several bands with different depolarization ratios, which means the presence of various aggregates of alcohol. The band of the stretching O—H vibration of water (symmetric and asymmetric vibrations) is also complex.

Calculations for multimolecular aggregates of pure methyl alcohol and pure water are given in Refs. [9–12].

Calculations showed that the band of the stretching O—H vibrations of CH_3OH really should be complicated. The fact is that in formation of H-bond the band of O—H vibrations is split, in some cases with changing the depolarization rations of the bands. For dimer O—H vibrations correspond to two bands with 4118.8 and 4192.7 cm^{-1} with almost identical depolarization ratios of 0.26–0.25. Accounting the large half-width of the bands and the presence of different H-aggregates these bands are not resolved experimentally in Raman spectra. Another picture holds for the trimeric aggregate. The band of O—H vibrations splits into three components of 4053.2 ($\Delta = 0.0998$), 4082.0 ($\Delta = 0.7091$) and 4087.9 ($\Delta = 0.7057$) cm^{-1}, the intensity of 4053.2 cm^{-1} band is the highest one. In the polarized component $I_{\parallel}$ this band should be manifested with the greatest intensity. In the perpendicular polarized component the bands 4082.5 and 4087.9 cm^{-1} should be manifested. These bands are not resolved by experimental apparatus, and they should be manifested in the experiment as a single broad band. Thus, the complexity of the band of O—H vibrations is confirmed by the results of calculation.

Let's consider, however, an aqueous solution of alcohol ($CH_3O\text{-}H\text{-}H_2O$). Because of the limited number of molecules in the calculations and excluding the thermal motion all water and alcohol molecules appeared to be H-bonded, but with some peculiarities. At low alcohol concentration alcohol molecules were pushed out of the water structure on the edge of the group. Molecules of alcohol appeared to be H-bonded with each other and also with water molecules of the outer structure but not with those in the bulk structure of water. This suggests that the solubility of the alcohol at low concentrations in the solution is bad and they are not pushed out due to H-bonds between themselves and a small number of water molecules. Structures of aggregates of 7 water molecules and 3 molecules of alcohol, as well as 3 water molecules and 7