Genetic algorithms for estimating the contributions of intramolecular resonances of water-ethanol solutions to the formation of their Raman spectra

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Raman spectroscopy is one of the most effective and informative methods for studying aqueous solutions of amphiphilic compounds. However, not all mechanisms of the formation of vibrational spectral bands of aqueous solutions of self-organizing amphiphiles have been fully elucidated. Therefore, it is not possible to obtain comprehensive information about interactions and oscillatory processes in systems from Raman spectra. Thus, the role of intramolecular Fermi resonances (IFR) and Darling-Dennison resonances (DDR) in the formation of the Raman spectrum of such self-organizing systems as e.g. water-ethanol solutions is unclear. This work is devoted to the study of the contributions of Raman scattering (RS) and DDR to the formation of spectral bands of water-ethanol solutions and of the influence of self-organization processes in the solutions on these contributions.

Water-ethanol solutions with ethanol concentrations of 20% and 70% by volume were used as objects of research when their temperature changed from -5 to 95 ^{o}C. According to [1], in the region with ethanol concentration of 20%, there is a significant strengthening of hydrogen bonds, as a result of which clathrate-like structures can form. With an ethanol content of 70% in aqueous ethanol solutions, sandwich-type clusters prevail [2]. To obtain useful precision information about the structure and processes of self–organization of amphiphiles in water from spectral bands, modern optimization methods were applied: BFGS modification of gradient descent algorithm combined with two modifications of the evolutionary method - genetic algorithms (GA): conventional GA (CGA) and its gender modification (GGA). A comparative analysis of the quality of decomposition of wide valence bands of OH groups of water and ethanol into Gaussian shaped components using BFGS, CGA+BFGS, and GGA+BFGS was carried out. It was established that the parameters of the interaction of RS and DDR are estimated with greater accuracy as a result of combination of GA and BFGS compared with use of BFGS only. Use of GGA instead of CGA does not improve the results.

Based on the analysis of experimental RS spectra using genetic algorithms, quantitative estimates of the IFR contribution to the intensity of the OH groups of valence bands of water and water-ethanol solutions were obtained. It was established that IFR contribution in aqueous solutions of micelle-forming compounds depends on the stages of self-organization. Analysis of the spectral band 5900 – 7450 cm^{-1} of water and water-ethanol solutions showed that the Darling-Dennison resonance (DDR) makes a decisive contribution to the formation of this band.

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