CALCULATION OF THE EFFECTIVE FREQUENCY OF POLARIZATION FLUCTUATIONS IN WATER

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In calculating the rate constants of reactions in polar liquids, the medium plays a dynamic role [1]. In the classical description of polarization fluctuations, the following expression can be written for the effective frequency:

$$\omega_{eff}^2 = \frac{2}{\pi c}\int_0^\infty d\omega\, \omega \frac{I_m \varepsilon(\omega)}{|\varepsilon(\omega)|^2}, \tag{1}$$

where $\varepsilon(\omega)$ is the complex permittivity, and the parameter c is equal to 0.543 for water. As can be seen from Eq. (1), the main contribution to ω_{eff} is made by high frequencies corresponding to the IR absorption region of water. Resonance formulas [1, 2] cannot be used to calculate ω_{eff} on the basis of Eq. (1), however, because the integral is divergent with respect to high frequencies. We have used the following approximation:

$$\frac{I_m \varepsilon(\omega)}{|\varepsilon(\omega)|^2} = \frac{c_R(\Gamma^2+\Omega_R^2)}{2\Omega_R}\left[\frac{\Gamma}{(\Omega_R-\omega)^2+\Gamma^2} - \frac{\Gamma}{(\Omega_R+\omega)^2+\Gamma^2}\right], \tag{2}$$

where c_R is equal to 0.377 for water. We found the resonance frequency Ω_R and the resonance width Γ from an analysis of experimental data [2]. As a result, we obtained a value of 10^{13} sec^{-1} for ω_{eff}. In addition, ω_{eff} was calculated by numerical integration using the experimental $I_m\varepsilon(\omega)$ curve. The resulting ω_{eff} value is practically the same as the result obtained above.

LITERATURE CITED

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