

The relation between dielectric and low frequency Raman spectra of hydrogen bond liquids

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In order to get deeper insights into dynamical properties of H-bond liquids that are embodied in the first and second rank dynamic susceptibilities and underlying molecular mechanisms, we have thoroughly analyzed the complex dielectric and low-frequency Raman spectra of water, methanol, and ethylene glycol at 25°C in microwave to THz frequency range. The dielectric spectra have been determined accurately using TDR [1], and combined with the data obtained by wave-guide interferometry [2,3], THz-TDS [4], and FIR [5,6], which achieves $\nu_{\max}=18\text{THz}$, 5THz, and 89GHz, respectively for these liquids. For reliable measurements of Raman spectra in the extremely low frequency region of $\nu/\text{cm}^{-1}\leq 2$ that is not accessible by a grating spectrometer, we employed a Fabry-Perot interferometer with the high resolution of 0.004 cm^{-1} .

As for water and methanol, the high frequency part of the dielectric spectrum deduced by a model-independent subtraction of the principal slow Debye relaxation term (τ_1) from the total spectrum clearly corresponds to the Raman spectrum (Fig.2). This means that the collective reorientational process specific to hydrogen bond liquids accompanied by huge dipole moment fluctuation is virtually not Raman active but both dynamic susceptibilities reflect the same molecular origins for the fast microscopic processes, such as a single or intra-molecular rotation, and intermolecular vibrations. In contrast, the Raman spectrum of ethylene glycol seems to exhibit the slow collective relaxation despite its small amplitude, indicative of the contribution of quadrupolar species arising from an internal flexibility of an ethylene glycol molecule.

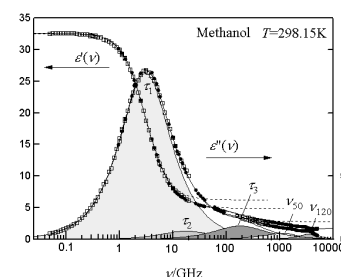


Fig.1 The complex dielectric spectrum of methanol in $50\text{MHz}\leq\nu\leq 5\text{THz}$.

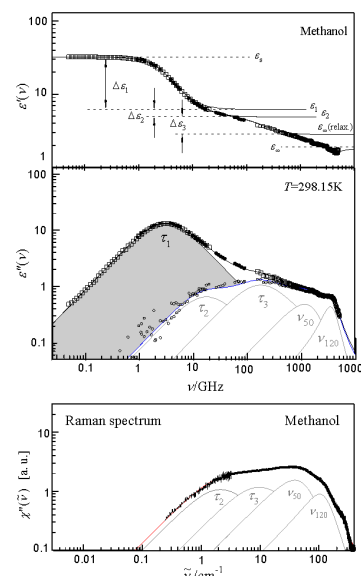


Fig.2 The comparison between dielectric and Raman spectra of methanol. Open symbols (\circ) represent the spectrum after subtraction of the principal relaxation term (τ_1) from the total spectrum.

References and note

- [1] T. Sato and R. Buchner, *J. Phys. Chem. A*, **108**, 5007 (2004).
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