Relation between macroscopic and microscopic dielectric relaxation times in water dynamics

Arkhipov V., Agmon N.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

A simplified derivation for the ratio of macroscopic to microscopic relaxation times of polar liquids is based on the Mori-Zwanzig projection-operator technique, with added statistical assumptions. We obtain several useful forms for the lifetime ratio, which we apply to the dynamics of liquid water. Our theoretical single-molecule relaxation times agree with the second Debye relaxation times as measured by frequency-domain dielectric spectroscopy of water and alcohols. From the theory, fast relaxation modes couple to the Debye relaxation time, τD, through very large water clusters, and their temperature dependence is similar to that of τD. Slower modes are localized to smaller water clusters and exhibit weaker temperature dependence. This is exemplified by the lifetime ratios measured by time-domain dielectric spectroscopy and optical Kerr effect spectroscopy, respectively.