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Raman spectra of water in the translational region: recent interpretation of experimental spectra and comparison with molecular dynamics simulations.

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Abstract: The comparison between experimental Raman spectra of water in the translational region and the molecular dynamics (MD) simulated ones has been performed. The specta can be interpreted in terms of long-range interaction-induced contributions.

Recent experimental studies of the Raman spectra of liquid water [1-3] have led to a new interpretation of its light scattering data in the low frequency region ($0<\nu<2000$ cm^{-1}). These papers have shown that most of isotropically scattered light can be interpreted in terms of long-range interaction-induced contributions, already found to dominate the spectra of non-hydrogen bond fluids [4]. In ref. 3 the isotropic spectrum was decomposed into two bands on the basis of its lineshape temperature dependence and isotopic effects on the librational dynamics. The low frequency component has the characteristic lineshape of long range interaction induced contribution and its integrated intensity decreases on lowering the temperature, as expected from trends in monoatomic fluid. The high frequency component centered around 800 cm^{-1} is librational in character and its intensity shows Arrhenius behaviour versus temperature, with an activation energy which suggest a close connection with hydrogen bond formation. In ref. 2 and 3 both the integrated intensity of the low-frequency isotropic component and the depolarization ratio of the entire experimental spectrum were compared with theoretical prediction

taking into account various induction mechanisms. Since theretical calculations can only be performed using crude approximations a test of the interpretation of the Raman spectrum via MD simulation is an urgent task.

Much effort has been devoted to computer simulation of liquid water based on pairwise additive model of the intermolecular potential, but only a few attempts have been made to simulate the Raman spectrum in the translational and librational region. We present an MD simulation of both the depolarized and isotropic spectra of water at different temperatures ($250<T<380$ K) and their comparison with experimental data [5,6]. We attempt to describe collision-induced scattering in the liquid phase by a multipolar and polarizability expansion in terms of isolated single-particle properties, following an established approch for simpler liquid [4].

The allowed spectrum is characterized by a broad band centered around 450 cm^{-1}, however its intensity is very low in comparison with the dipole-induced dipole between isotropic scatterers (IDID) spectrum. Indeed the latter dominates the depolarized spectrum [5,6].

As far as the isotropic spectrum is concerned, the excellent agreement between the simulated spectrum (considering the contribution originating by higer order polarizability and hyperpolarizability contributions)and the experimental low-frequency spectral shape support that its low frequency contribution is due to long range interaction-induced scattering.

3. References

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