

Time-Domain Calculations of the Polarized Raman Spectra and the Transient IR Absorption Anisotropy of the OH Stretching Mode of Liquid Water

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A time-domain method for calculating vibrational band profiles that simultaneously takes into account both the diagonal frequency modulations (of individual oscillators in the system) and the off-diagonal (intermolecular) vibrational coupling is developed and applied to the OH stretching band of liquid water (neat liquid H₂O). It is shown that the calculated spectral features of both the isotropic and anisotropic Raman bands, including their temperature dependence, are in reasonable agreement with the experimental results [1]. The time dependence of the transient IR absorption anisotropy is also calculated with a previously developed method [2]. The calculated decay of the transient IR absorption anisotropy is very fast (~100 fs) for neat liquid H₂O, while it is much slower (~600 fs) for a dilute solution of H₂O (and HDO) in D₂O, which is also in reasonable agreement with the experimental results [3, 4]. The time-domain behavior of the extent of delocalization of the vibrational mode is calculated. The OH stretching mode becomes delocalized over ~10 molecules (~20 oscillators) in about 550 fs. This result is compared to the cases of the C=O stretching modes of liquid acetone [5] and N,N-dimethylformamide (DMF) [6]. It is shown that the vibrational modes become delocalized more quickly as the magnitude of the noncoincidence effect (the frequency separation between the first moments of the isotropic and anisotropic Raman bands) becomes larger.

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