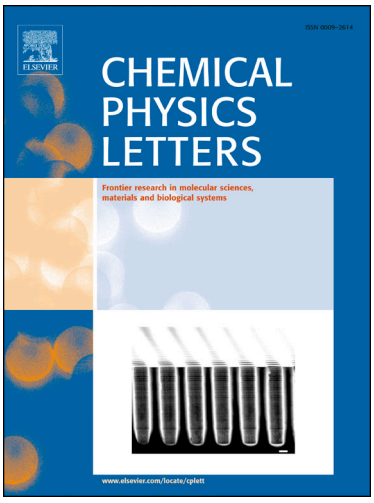

Frontiers article

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Isolation of site-specific anharmonicities of individual water molecules in the $I^-\cdot(H_2O)_2$ complex using tag-free, isotopomer selective IR-IR double resonance

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Abstract

We reveal the microscopic mechanics of iodide ion microhydration by recording the isotopomer-selective vibrational spectra of the $I^-\cdot(H_2O)\cdot(D_2O)$, $I^-\cdot(HOD)\cdot(D_2O)$, and $I^-\cdot(DOH)\cdot(H_2O)$ isotopologues using a new class of ion spectrometer that is optimized to carry out two-color, IR-IR photodissociation in a variety of pump-probe schemes. Using one of these, we record the linear absorption spectra of a cryogenically cooled cluster without the use of a messenger "tag". In another protocol, we reveal the spectra of individual H_2O and D_2O molecules embedded in each of the two possible binding sites in the iodide dihydrate, as well as the bands due to individual OH and OD groups in each of the four local binding environments. Finally, we demonstrate how temperature dependent isotopic scrambling among the spectral features can be used to monitor the onset of large amplitude motion, heretofore inferred from changes in the envelope of the OH stretching vibrational manifold.

Key Words: vibrational spectroscopy, ions, water, halide, IR-IR double resonance

Highlights:

- Tag-free IR2PD linear spectrum
- Excited molecule spectrum
- Identification of local OH oscillators
- Intermolecular and intramolecular coupling between H_2O molecules
- Multiple resonance laser spectroscopy