Synopsis of Original Research Paper

Elucidation of the environment of hydrated water at the molecular level using terahertz spectroscopy

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Terahertz (THz) spectroscopy has become an increasingly popular technique for probing the properties of a wide range of materials and compounds. Extensive inter- and intramolecular vibrations in the low-frequency THz energy region are expected in molecular crystals. The intermolecular vibrational modes in these crystals are non-localized but are of a collective (phonon-like) nature and are regarded as lattice vibrations. We have investigated the anomalous temperature-dependent upward frequency shift due to electron–phonon (e–p) polar-coupling interactions in thiamin chloride hydrochloride monohydrate crystal, focusing on the open cavities within the crystal. These open cavities are located around two methyl groups and one of two chlorine atoms that are close to each other, with the chlorine atom and one of the methyl groups connected to the hydration water. X-ray crystallography and first-principles calculations reveal that the key structure for the e–p polar-coupling interaction is an open cavity near the considered vibration. The vibrational modes assigned to temperature-dependent blue-shifted peaks exhibit large atomic displacements near the open cavity. Analysis of the temperature-dependent frequency shift proportional to the Bose–Einstein statistical factors based on the quantum mechanical description revealed that the strength of the e–p polar-coupling interaction and the frequency of the phonons interacting with the electrons were 5.3×10^{-3} cm^{-1} K^{-1} and 76.6 cm^{-1}, respectively. Interestingly, in the same crystal, the e–p interaction strength was similar for both polar coupling and multiphonon scattering. Phonon dispersion curves exhibiting LO (longitudinal optical) – TO (transverse optical) splitting confirmed that the highest frequency LO phonon participates in the polar-coupling interaction. Our results suggest that open cavities are essential for generating e – p polar-coupling interactions in crystals. The current study to interpret the temperature-dependent upward frequency shift is still preliminary, and future studies will require further accumulation of data on this phenomenon.