

VIBRATIONAL SPECTROSCOPY OF THE COPPER(I) CATION-DIHYDROGEN COMPLEXES AND THEIR ISOTOPLOGUES

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Porous materials containing under-coordinated Cu(I) centers can play an important role in dihydrogen adsorption as well as the efficient isotope separation of H₂/D₂. The vibrational spectra of the copper(I) cation–dihydrogen complexes of Cu⁺(H₂)₄ and Cu⁺(H₂O)(H₂)₂, as well as their isotopologues, Cu⁺(D₂)₄, Cu⁺(D₂)₃(H₂)₁, Cu⁺(H₂O)(D₂)₂, Cu⁺(D₂O)(H₂)₂ and Cu⁺(D₂O)(D₂)₂ are therefore studied using cryogenic ion trap vibrational spectroscopy in combination with quantum chemical calculations, for an in-depth understanding of the binding nature between dihydrogen and under-coordinated copper(I) cation complexes. The infrared photodissociation (IRPD) spectra measured in the HH (or DD) stretch regions (2500 cm⁻¹ to 4400 cm⁻¹) are assigned based on the calculated frequencies using vibrational second-order perturbation theory (VPT2). The observed vibrational features are attributed to the excitations of dihydrogen stretching fundamentals (ν_{HH}) and combination bands of these fundamentals with low-frequency mode excitations. The ν_{HH} frequencies in Cu⁺(H₂)₄ shows large red-shifts by 432 cm⁻¹ relative to the frequency of a free H₂ molecule (4161 cm⁻¹), indicating a stronger bonding of dihydrogen to the Cu(I) center.^a The ν_{HH} shift is even larger in Cu⁺(D₂O)(H₂)₂ cation, due to the presence of the water molecule. The studies of isotopologues and the combination bands reveal that the anharmonic effect plays a profound role in the vibrational spectra and the thermodynamic properties. Further, the non-ergodic dissociation behavior in the Cu⁺(D₂)₃(H₂)₁ and a fluxional nature are discussed.

^aJin et.al., Phys. Chem. Chem. Phys., 2023, 25, 5262.