

UNRAVELING HYDROGEN-BONDING INTERACTION, FERMI RESONANCES AND SOFT-MODE COUPLING
IN PHENOL-BENZIMIDAZOLE PROTON-COUPLED ELECTRON TRANSFER MODEL COMPLEXES WITH
CRYOGENIC ION VIBRATIONAL SPECTROSCOPY

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Proton-coupled electron transfer (PCET) has been of great interest in chemical and biochemical catalysis. The electron transfer process in numerous biomimetic systems has been investigated in solution, but direct interrogation of the proton transfer coordinate remains largely unexplored. We have measured cryogenic ion vibrational spectra of a series of phenol-benzimidazole PCET model compounds to explore the nature of the strong OH—N H-bond in the ground electronic state. Highly redshifted and broadened H-bonded OH stretch transitions were observed throughout the model series. Isotopic substitution and anharmonic vibrational calculations suggest that the breadth arises from an interplay between strong OH stretch-bend Fermi resonance interactions and coupling of the OH stretch to low frequency H-bond soft-mode motions accessible at the zero-point level. The effects of steric hindrance, resonance stabilization and charge distribution are also investigated through systematic structural variation of the model compounds.