Proton-coupled electron transfer (PCET) processes are vitally important throughout chemical and biochemical catalysis. While electron transfer kinetics have been well studied, direct interrogation of the proton transfer coordinate has remained largely unexplored. We present cryogenic ion vibrational spectra of a series of phenol-benzimidazole and phenol-pyridine PCET model dyads to explore the nature of the strong OH—N H-bond in the ground electronic state. Highly red shifted and asymmetrically broadened H-bonded OH stretch transitions are observed throughout the model series, while the deuterated isotopologues yield much weaker OD stretch transitions that are more symmetrically broadened. To explain the origins of the spectral broadening, we employ a computational model that couples the two-dimensional potentials describing the stretching and in-plane bending degrees of freedom of the shared H atom to the remaining vibrational degrees of freedom. These two-dimensional potentials are predicted to be very shallow along the H atom transfer coordinate, enabling significant dislocation of the H atom between the donor and acceptor groups upon excitation of the OH vibrational modes. These soft H atom potentials result in strong coupling between the OH modes, which exhibit extensive bend-stretch mixing, and a large number of normal mode coordinates. Vibrational spectra are calculated using a Hamiltonian that linearly and quadratically couples the H atom potentials to over thirty of the most strongly coupled normal modes treated at the harmonic level. The calculated vibrational spectra qualitatively reproduce the shape and breadth of the experimentally observed bands in both isotopologues. The results highlight a unique broadening mechanism and complicated anharmonic effects present within these biologically relevant PCET model systems.