TUNNELING IN A REDUCED DIMENSIONAL MODEL OF H_5^+

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The H_5^+ molecular ion has been studied since the 1960s due to its role as the product of H_2 + H_3^+ collisions, which is of astrochemical relevance as an intermediate in the interstellar production of HD. Since the mid-1980s, much experimental and theoretical effort has gone into both obtaining and simulating the IR absorption spectrum of H_5^+. Multiple assignments for the observed peaks have been proposed, from those resulting from very simple harmonic treatments to those arising from full-dimensional multi-configuration time-dependent Hatree (MCTDH) calculations. This full-dimensional MCTDH approach, while in excellent agreement with experimental energies and intensities, poses a challenge to assignment as it does not directly provide eigenfunctions of the vibrational Hamiltonian.

Motivated by newly recorded spectra of H_5^+ and D_5^+ between 4500 and 7500 cm^{-1}, we have developed an alternate approach, based on a four-dimensional Hamiltonian that is adiabatically separated into a pair of coupled two-dimensional Hamiltonians whose eigenfunctions may be directly calculated by a discrete variable representation. This approach has the benefit of providing good agreement with experiment, while dramatically simplifying the assignment of the transitions. After assignment, it became clear that the progressions of peaks observed in the IR spectrum of H_5^+ arise from the effects of proton tunneling between two configurations of the system that look like $H_2{\cdot}H_3^+$ and $H_3^+{\cdot}H_2$ respectively. This tunneling behavior is further demonstrated by the analysis of a one-dimensional model Hamiltonian with non-adiabatic couplings. This treatment has also been applied to the deuterated isotoplogues D_5^+, $H_2D^+H_2$, and $D_2H^+D_2$ with each system displaying the same tunneling behavior, but with differences in the length of the progression supported.