SPECTROSCOPIC SIGNATURES OF LARGE AMPLITUDE VIBRATIONAL MOTIONS IN $H_5O_2^+$ AND $H_3O_2^-$

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Recent spectroscopic studies of $H_5O_2^+$[a,b,c] and $H_3O_2^-$[d,e] in the 600 - 2000 cm^{-1} region have displayed strong transitions at frequencies that do not correlate to any of the expected harmonic vibrational frequencies in these systems. In this talk we will present results of calculations of the transition frequencies and intenisties using Diffusion Monte Carlo and variational calculations, performed using *MULTIMODE*.[f] For these studies, we employ fully *ab initio* potential surfaces, recently reported by Huang, Braams and Bowman.[g] Excellent agreement between the experimental and calculated spectra are obtained for both species. We find that the fact that the transitions frequencies are shifted by as much as several hundred cm^{-1} from the corresponding harmonic values is evidence of strong coupling among the zero-order normal mode vibrations as well as very large amplitude vibrational motions, even at relatively low levels of vibrational excitation.

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