REVISITING THE INFRARED SPECTRUM OF MONODEUTERATED HYDRONIUM, H_2DO^+

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The infrared laser direct absorption spectroscopy of H_2DO^+ in the OH stretching region has been recently reported[a] which revealed large amplitude tunneling dynamics similar to the isoelectronic NH_2D species. The large rotational constants make the jet cooled spectrum relatively sparse at low rotational temperatures. This, together with the large asymmetry of the molecule ($\kappa = -0.2616$), makes assignments more challenging. Transitions are assigned through 4-line ground state combination differences (GSCDs), with additional tentative assignments made via comparison of predicted/observed spectra and yielding a total of 24 GSCDs. Quite recently, Furuya et al.[b] reported on 9 rotation-inversion transitions measured in the millimeter and submillimeter regions, which, when fit to a 9-parameter Hamiltonian, yield tunneling splittings and rotational constants differing slightly from IR fit predictions. This has prompted the present reinvestigation of the H_2DO^+ spectra, which now takes advantage of combined data from both the infrared and mm wave studies, and permits many additional lines in the infrared OH stretch spectrum to be assigned and confirmed by 2-line combination differences. The analysis is based on a Hamiltonian model for the well studied NH_2D molecule, modified to account for the larger tunneling splitting. The process is still underway, but has already allowed us to extend the IR line list considerably, with both infrared and mm wave data now fitting well within experimental uncertainties. The combined analysis of both IR and mm wave spectral data leads to improvement in parameters for both the ground and OH stretch vibrationally excited states of this important molecular ion, as well as provides guidance for spectral search in the OD stretch region.

[a] F. Dong and D. J. Nesbitt, *J. Chem. Phys.* **125** (2006) Art. No. 144311.
[b] T. Furuya, S. Saito, and M. Araki, *J. Chem. Phys.* **127** (2007) Art. No. 244314.