# ACCURATE MEASUREMENTS OF THE $J = 1 - 0$ TRANSITIONS OF $H_2D^+$ AND $HD_2^+$ USING LASER-INDUCED REACTIONS AND DETERMINATION OF SPECTROSCOPIC PARAMETERS FOR $H_2D^+$

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The method of laser-induced reaction[a] has been used for the first time to detect rotational transitions. The astronomically important $1_{01} - 0_{00}$ and $1_{11} - 0_{00}$ transitions of $H_2D^+$ and $HD_2^+$, respectively, have been recorded by observing the enhancement of their D/H isotope exchange reactions with $p$-$H_2$ upon rotational excitation in a cryogenic multipole ion trap. While the frequency for $HD_2^+$ is in good agreement with a previous, unpublished result,[b] but more accurate, the frequency for $H_2D^+$ is some 60 MHz lower than the value from the same unpublished source (*b*).

The present $H_2D^+$ frequency has been fit together with previously published pure rotational transitions and with infrared ground state combination differences (GSCDs).[c] Starting values for spectroscopic parameters were derived from energies up to $J = K_a = 7$ calculated ab initio[d] because of the smallness of the data set. Since the molecular ion is fairly floppy, the Hamiltonian has been expanded in Euler functions[e] up to 6th order. Omitting one GSCD because of a large residual, the remaining GSCDs were reproduced to almost $0.002\,\mathrm{cm}^{-1}$ releasing only 7 parameters. Thus, for the first time this IR spectroscopic data has been reproduced within experimental uncertainties. The pure rotational transitions were fit overall within the reported experimental uncertainties. In Ref. *c* the wrong $1_{01} - 0_{00}$ transition frequency required 11 parameters to fit the pure rotational transitions within experimental uncertainties, albeit with somewhat larger residuals for the GSCDs than in the present work.

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[a] E. g. O. Asvany et al., *J. Chem. Phys.* **127** (2007) Art. No. 154317.
[b] D. A. Jennings et al.; cited in T. Amano and T. Hirao, *J. Mol. Spectrosc.* **233** (2005) 7.
[c] Summarized in T. Amano, *Phil. Trans. R. Soc. A* **364** (2006) 2943.
[d] O. L. Polyansky et al., *J. Mol. Spectrosc.* **157** (1993) 237; J. Ramanlal and J. Tennyson, *Mon. Not. R. Astron. Soc.* **354** (2004) 161.
[e] H. M. Pickett et al., *J. Mol. Spectrosc.* **233** (2005) 174.