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Astrophysically motivated laboratory measurements of deuterium reacting with isotopologues of H_3^+

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Abstract. H_2D^+ and D_2H^+ are important chemical tracers of prestellar cores due to their pure rotational spectra that can be excited at the ~ 20 K temperature of these environments. The use of these molecules as probes of prestellar cores requires understanding the chemistry that forms and destroys these molecules. Of the eight key reactions that have been identified (Albertsson *et al.* 2013), five are thought to be well understood. The remaining three are the isotope exchange reactions of atomic D with H_3^+, H_2D^+, and D_2H^+. Semi-classical results differ from the classical Langevin calculations by an order of magnitude (Moyano *et al.* 2004). To resolve this discrepancy, we have carried out laboratory measurements for these three reactions. Absolute cross sections were measured using a dual-source, merged fast-beams apparatus for relative collision energies between ~ 10 meV to ~ 10 eV (Hillenbrand *et al.* 2019). A semi-empirical model was developed incorporating high level quantum mechanical *ab initio* calculations for the zero-point-energy-corrected potential energy barrier in order to generate thermal rate coefficients for astrochemical models. Based on our studies, we find that these three reactions proceed too slowly at prestellar core temperatures to play a significant role in the deuteration of H_3^+ isotopologues.

Keywords. astrochemistry, ISM: molecules, methods: laboratory, molecular data, molecular processes

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H_3^+ and its isotopologues play an important role in the dynamics of prestellar cores. At the densities and temperatures typical for prestellar cores, most molecules freeze onto dust grains (van der Tak 2006). A notable exception is H_3^+ and its isotopologues, which become the dominant positive charge carriers in the gas, coupling the gas to any ambient magnetic fields and thereby affecting core collapse (Kong *et al.* 2015). For this reason, it is highly desirable to know the total abundance of H_3^+ and its isotopologues within a prestellar core. However, the symmetric H_3^+ and D_3^+ have no pure rotational spectra that can be excited at prestellar core temperatures, and thus cannot be directly observed. This is to be contrasted with H_2D^+ and D_2H^+, which have pure rotational spectra that can be excited at prestellar core temperatures, rendering them directly observable.

Using H_2D^+ and D_2H^+ to probe prestellar cores and infer the total abundance of the H_3^+ isotopologues requires understanding the chemistry that forms and destroys these molecules. Collisions with D, HD, and D_2 are predicted to be the most important astrochemical reactions that deuterate H_3^+, H_2D^+, and D_2H^+, forming H_2D^+, D_2H^+, and D_3^+,

respectively (Albertsson *et al.* 2013). Reactions with HD and D_2 are considered relatively well understood experimentally and theoretically (Adams & Smith 1981; Gerlich *et al.* 2002; Gerlich & Schlemmer 2002; Giles *et al.* 1992; Hugo *et al.* 2009). However, there are no experimental measurements for deuterating reactions with atomic D. Moreover, the only published theoretical cross sections (Moyano *et al.* 2004) have been found to have several chemical inconsistencies (Hillenbrand *et al.* 2019).

To address this issue, we have carried out laboratory measurements for the three H_3^+ isotopologues that undergo isotope exchange reactions with atomic D. We have used our dual-source, merged-beams apparatus (O'Connor *et al.* 2015; de Ruette *et al.* 2016) to measure absolute integral cross sections for relative collision energies ranging from ~ 10 meV to ~ 10 eV (Hillenbrand *et al.* 2019). In addition, high level quantum mechanical *ab initio* calculations were performed to model the zero-point-energy corrected energy profiles and refine the predicted potential energy barrier. From the combined experimental and theoretical data, a semi-empirical model was developed to generate thermal rate coefficients for the reactions of D with isotopologues of H_3^+, for use in astrochemical models.

Our combined theoretical and experimental results find that there is a reaction barrier of ~ 800 K for the deuterating reactions studied here. Thus, in the absence of tunneling, these reactions do not proceed at prestellar core temperatures. Taking into account the effect of tunneling results in rate coefficients of $< 10^{-13}$ cm^3 s^{-1} for temperatures below 20 K. Hence, even with tunneling, these reactions proceed too slowly to be important at prestellar core temperatures. Based on our findings and the work of others (Hugo *et al.* 2009; Albertsson *et al.* 2013), we conclude that reactions wth HD are the primary reactions that deuterate the isotopologues of H_3^+ in prestellar cores. More details on our findings can be found in Hillenbrand *et al.* (2019) and Bowen *et al.* (in prep).

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