Astrochemically motivated experimental and theoretical studies of isotope exchange reactions between D and isotopologues of H_3^+

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Synopsis We present astrochemically motivated experimental studies for the isotope exchange reactions of H_3^+, H_2D^+, and D_2H^+ colliding with atomic D forming H_2D^+, D_2H^+, and D_3^+, respectively. For these reactions we performed cross section measurements using our merged-beams apparatus. In addition, we carried out theoretical calculations of the zero-point-corrected energy profiles. From our results we derive thermal rate coefficients over the temperature range relevant for astrochemical models.

The H_3^+ molecule, and its isotopologues H_2D^+ and D_2H^+, are some of the most prominent molecular ions in the field of astrochemistry, which aims to describe the formation of stars and planets from interstellar molecular clouds. In particular, at the densities of $\sim 10^6$ cm^{-3} and temperatures of ~ 20 K typical for prestellar cores, most molecules freeze onto dust grains. 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 the dynamics of the core collapse. The symmetric H_3^+ and D_3^+ have no pure rotational spectrum and are therefore not observable in prestellar cores. This is to be contrasted with H_2D^+ and D_2H^+, which have a pure rotational spectrum that can be excited at prestellar core temperatures. However, using H_2D^+ and D_2H^+ to probe prestellar cores and to infer the total abundance of H_3^+ isotopologues requires understanding the chemistry that forms and destroys these molecules.

Deuteration of H_3^+, H_2D^+, and D_2H^+ forming H_2D^+, D_2H^+, and D_3^+, respectively, can occur either in collisions with atomic D or with the diatomic molecules HD and D_2. The latter two cases are considered to be well understood through experimental and theoretical studies, and the results have been implemented into astrochemical models [1]. In contrast, the role of deuteration through collisions with atomic D remains an open question in astrochemistry. Previously published theoretical cross sections showed inconsistencies [2] and have not been adopted into astrochemical models up to now.

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 fast-beams apparatus, which enables us to study reactions of neutral atoms and molecular ions [3]. Co-propagating beams allow us to measure absolute total cross sections for relative collision energies ranging from ~ 10 meV to ~ 10 eV. In addition, high level quantum *ab initio* calculations have been carried out to model the zero-point-energy corrected energy profile and the shape of the potential energy barrier, allowing an evaluation of the tunneling effects. From the combination of experimental and theoretical results we derive thermal rate coefficients over the temperature range relevant for astrochemical models [4].

References

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