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$_2$D$^+$, and D$_2$H$^+$ colliding with atomic D forming H$_2$D$^+$, D$_2$H$^+$, 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$_2$D$^+$ and D$_2$H$^+$, 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 $\sim 20$ 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$_2$D$^+$ and D$_3^+$ have no pure rotational spectrum and are therefore not observable in prestellar cores. This is to be contrasted with H$_2$D$^+$ and D$_2$H$^+$, which have a pure rotational spectrum that can be excited at prestellar core temperatures. However, using H$_2$D$^+$ and D$_2$H$^+$ 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$_2$D$^+$, and D$_2$H$^+$ forming H$_2$D$^+$, D$_2$H$^+$, 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 $\sim 10$ meV to $\sim 10$ 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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