Low-energy reactive collisions of H_2, HD, and D_2 with H_2^+, HD^+, D_2^+: branching ratios, deviation from Langevin behavior and kinetic energy analysis of the products.

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The study of low-temperature collisions between small molecules, molecular hydrogen in particular, is crucial to understand the chemistry of interstellar clouds, characterized by temperatures typically in the 3 K to 60 K range. These studies can also be used to test theoretical predictions about the reaction rates, the product branching ratios, and the product kinetic-energy distributions [1]. The ion-molecule capture rates are well described by the semi-classical Langevin theory at high to moderate energy, but deviations at low energies are predicted, and experimentally observed [1,2,3].

Low-energy collisions of molecules with ions are difficult to study because stray fields heat the ions up. This difficulty is circumvented by replacing the ions with the corresponding parent neutral molecule in highly excited Rydberg states. The Rydberg electron, very far from the core and loosely bound, shields the ion core from external fields while having negligible impact on its reactions with neutral molecules located within the Rydberg-electron orbit [3,4]. To reach low collision energies, velocity-tunable supersonic beams of the reactants are merged.

Rydberg-Stark states are produced in one of the two beams by photoexcitation in the presence of an electric field and subsequently velocity selected and deflected using a curved chip-based surface-electrode deflector [5]. This deflector exploits the very large dipole moments of Rydberg-Stark states and allows us to merge the Rydberg molecular beam with a supersonic beam of the ground-state neutral molecules. The relative and absolute axial velocities of the reactants can also be varied by adjusting the velocity selected by the deflector, by varying the delays between the openings of the valves, and by changing their temperatures. The longitudinal velocity spread of the molecular beams rapidly evolve into a spatial dispersion, which enables a high collision-energy resolution and studies at collision energies below $k_B \cdot 1$ K, where the reaction rates are enhanced relative to the Langevin capture rate for a pure ion─induced-dipole interaction [1,2].

We report on experimental studies of low-energy ion-molecule reactions between the neutral molecules H_2, HD, and D_2 and the molecular ions H_2^+, HD^+, D_2^+. Differences resulting from nuclear-spin symmetry were investigated by exchanging natural H_2 with *para*-enriched H_2. These studies allow systematic quantitative analysis of the enhancement effect for systems of different reduced masses and rotational-state occupations of the ground-state reactant. The observations can be explained be explained by ion─quadrupole interaction and quantum-capture contributions. The studies also allow the determination of the branching ratios between different product channels, i. e., $H_2D^+ + H$ and $H_3^+ + D$ in the reaction of H_2 with HD^+, to test simple theoretical models, such as a combinatorial model, a model describing the reactions as H-, H^+-, D-, and D^+-transfer processes, and a statistical model relating the reaction rate coefficients to the translational and rovibrational state densities of the product channels.

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