

THE LOW-TEMPERATURE NUCLEAR SPIN EQUILIBRIUM OF H_3^+ IN COLLISIONS WITH H_2

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Observations of H_3^+ in diffuse molecular clouds have revealed that the ratio of its *ortho* and *para* nuclear spin modifications are not in thermodynamic equilibrium with the environment. This discrepancy could be explained if the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$, which interconverts the nuclear spin modifications of H_3^+ , has a nonthermal outcome at low temperatures, possibly arising from nuclear spin selection rules on systems of identical fermions. While the nuclear spin dependence of this reaction has previously been investigated experimentally, the prior measurements were limited to temperatures above ~ 130 K, well above the 50-70 K typical of diffuse molecular clouds.

To investigate whether the outcome of the $\text{H}_3^+ + \text{H}_2$ reaction is nonthermal, H_3^+ ions were allowed to interact with H_2 in the temperature-controlled environment of a 22-pole radiofrequency ion trap, and the relative abundances of *ortho*- and *para*- H_3^+ at steady state were measured using action spectroscopy. By carefully controlling the *ortho:para* ratio of the H_2 samples in conjunction with the ion trap temperature, the outcome of the reaction was observed to be close to thermodynamic equilibrium over the temperature range of 45-100 K. Thus, the nonequilibrium *ortho:para* ratio of H_3^+ observed in diffuse molecular clouds does not arise from a nonthermal outcome of the $\text{H}_3^+ + \text{H}_2$ reaction at low temperature. This implies that the origin of the discrepancy lies in the respective formation and destruction mechanisms of H_3^+ .

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