

OBSERVATION OF NUCLEAR SPIN SELECTION RULES IN SUPERSONICALLY EXPANDING PLASMAS CONTAINING H_3^+

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The reaction of $\textit{para}\text{-H}_2^+$ with $\textit{para}\text{-H}_2$ can form only the \textit{para} spin modification of H_3^+ , according to nuclear spin selection rules. A proton hop from $\textit{para}\text{-H}_3^+$ to $\textit{para}\text{-H}_2$ maintains the $\textit{para}\text{-H}_3^+$, but a hydrogen exchange reaction can produce $\textit{ortho}\text{-H}_3^+$. In the hopes of developing a source of H_3^+ that is almost entirely in a single quantum state ($J = K = 1$), we have investigated a supersonically expanding plasma using a pulsed discharge nozzle with pure $\textit{para}\text{-H}_2$ as a precursor gas. The plasma has been interrogated via continuous-wave cavity ringdown spectroscopy using a homemade difference frequency laser that combines a tunable Ti:Sapphire laser and a fixed frequency Nd:YAG laser. With this system, we have measured the relative intensities of the $R(1, 0)$, $R(1, 1)^u$, and $R(2, 2)^l$ transitions of the ν_2 band of H_3^+ near $3.67\ \mu\text{m}$.

We will discuss the construction of the difference frequency laser, our adaptation of continuous-wave cavity ringdown spectroscopy to a pulsed source, and the results of our spectroscopic study. We have found that it is possible to produce highly enriched $\textit{para}\text{-H}_3^+$, especially when an inert gas is used as a buffer to reduce the rate of reactions between H_3^+ and H_2 . We have also found that the ratio between the rate coefficients of the proton hop and hydrogen exchange reactions $\alpha = k_H/k_E \sim 1$ at the low temperatures of our expansion, in contrast to the value of $\alpha \sim 2.4$ found by the Oka group^a at the higher temperatures of a water-cooled hollow cathode discharge.

^aM. Cordonnier, D. Uy, R. M. Dickson, K. E. Kerr, Y. Zhang, and T. Oka *J. Chem. Phys.* **113**, 3181 2000.