# SPECTROSCOPIC MEASUREMENTS OF THE REACTION $H_3^+ + H_2 \rightarrow H_2 + H_3^+$

KYLE N. CRABTREE, CARRIE A. KAUFFMAN, BRIAN A. TOM,[a] EFTALDA BEÇKA, BRETT A. McGUIRE,[b] BENJAMIN J. McCALL, *Department of Chemistry, University of Illinois, Urbana, IL 61801, USA.*

The fundamental reaction involving $H_3^+$ and $H_2$ has not been well-studied in the laboratory. Typical approaches to studying kinetics using mass spectrometry are ineffective because the products have identical masses to the reactants. Isotopic labeling fundamentally alters the exchange symmetry of this system, and therefore cannot be employed. However, because the two nuclear spin configurations of $H_3^+$ (*ortho*, $I = 3/2$, and *para*, $I = 1/2$) and $H_2$ (*ortho*, $I = 1$, and *para*, $I = 0$) are linked to specific rotational states by symmetry, spectroscopy is a useful tool for studying this reaction.

We have employed infrared multipass direct absorption spectroscopy to measure transitions in the $\nu_2$ fundamental band of $H_3^+$ using a difference frequency generation laser. Hydrogenic plasmas were produced in a hollow cathode discharge cell, which could be cooled as low as 130 K using liquid nitrogen. To measure the nuclear spin dependence of the $H_3^+ + H_2$ reaction, we prepared hydrogen gas enriched up to 99.9% *para*-$H_2$ using a *para*-hydrogen converter, and determined the *ortho:para* ratio of $H_3^+$ formed in the hollow cathode plasma at steady state as a function of both *para*-hydrogen enrichment and temperature. By utilizing steady state chemical models, we have determined that the ratio of the rates of the proton hop and hydrogen exchange pathways ($\alpha \equiv k^H/k^E$) decreases from $1.6 \pm 0.1$ at 350 K to $0.5 \pm 0.1$ at 135 K. These results suggest that at lower temperatures, the intermediate $(H_5^+)^*$ complex lifetime increases, leading to more statistical proton scrambling.

[a] Present Address: Department of Chemistry, United States Air Force Academy, Air Force Academy, CO 80840, USA

[b] Present Address: Department of Chemistry, Emory University, Atlanta, GA 30322, USA