INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE REACTION $H_3^+ + CO \rightarrow H_2 + HCO^+/HOC^+$

TSUNEO HIRANO, *Department of Chemistry, Faculty of Science, Ochanomizu University, Tokyo 112-8610, Japan*; HUI LI, ROBERT J. LE ROY, and TAKAYOSHI AMANO, *Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*.

Observations of the rotational lines of HCO^+ produced in an extended negative glow discharge revealed high vibrational temperatures for the stretching vibrational modes, and non-thermal population distributions among the different ℓ levels of excited bending vibrational states.[a,b] These results provide critical tests of our understanding of the dynamics and intramolecular vibrational energy redistribution (IVR) in this reaction process. The IVR in the HNC $\leftrightarrow$ HCN isomerization reaction[c] has been studied previously by *ab initio* direct dynamics and vibration-mapping[d] methods. An extension of the method used for the HNC/HCN isomerization reaction yields a new procedure for studying "IVR in reactions" which is applied to HCO^+/HOC^+ production in the H_3^+ + CO reaction, as described by the five-dimensional potential energy surface and pathways for this reaction reported recently by Li *et al.*[e]
Dynamics calculations have been performed for "co-linear configuration" reactions in which H_3^+ approaches the C end of CO with a translational temperature of 20 K (a typical kinetic temperature of dark clouds) or 330 K (a typical translational temperature for ions in a glow discharge). As H_3^+ approaches CO with the lower-temperature translational energy, the hopping of H^+ to the CO moiety to form HCO^+ occurs over a period of about 100 fs, and the H–C stretching mode of the product HCO^+ is highly excited. This excitation can relax within the same vibrational ladder and/or be transferred to the bending mode through anharmonic coupling. Details of direct dynamics calculations for this process will be reported.

[a] T. Hirao, S. Yu, and T. Amano, *J. Chem. Phys.*, **127**, 074301 (2007).
[b] T. Hirao, S. Yu, and T. Amano, *J. Mol. Spectrosc.*, **248**, 26 (2008).
[c] Y. Kumeda, Y. Minami, K. Takano, T. Taketsugu, and T. Hirano, *J. Mol. Struct. (THEOCHEM)*, **458**, 285 (1999)
[d] T. Hirano, T. Taketsugu, and Y. Kurita, *J. Phys. Chem.*, **98**, 6936 (1994).
[e] H. Li, T. Hirano, T. Amano, and R.J. Le Roy, *J. Chem. Phys.*, **129**, 244306 (2008).