INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE REACTION
H₂⁺ + CO → H₂ + HCO⁺/HOC⁺

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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. 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 ↔ HCN isomerization reaction has been studied previously by ab initio direct dynamics and vibration-mapping 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 H₂⁺ + CO reaction, as described by the five-dimensional potential energy surface and pathways for this reaction reported recently by Li et al. Dynamics calculations have been performed for “co-linear configuration” reactions in which H₂⁺ 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 H₂⁺ 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.

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