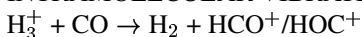


INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE REACTION



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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.^{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 $\text{HNC} \leftrightarrow \text{HCN}$ 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 $\text{HCO}^+/\text{HOC}^+$ production in the $\text{H}_3^+ + \text{CO}$ 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.

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