INFRARED ACTION SPECTROSCOPY AND TIME-RESOLVED DYNAMICS OF THE OD-CO REACTANT COMPLEX

ILANA B. POLLACK, MARIA TSIOURIS, HELEN O. LEUNG,[a] AND MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

Infrared action spectra of the linear OD-CO reactant complex have been recorded in the OD overtone region near 1.9 μm using an infrared pump-ultraviolet probe technique. The pure overtone band of OD-CO ($2\nu_{\mathrm{OD}}$) was observed at 5148.4 cm^{-1}, and combination bands involving the simultaneous excitation of OD stretch and D-atom bend were identified 200.7 and 232.1 cm^{-1} to higher energy. Band assignments and spectroscopic constants have been derived from the rotationally resolved structure of the spectra. Direct time-domain measurements yielded a lifetime of 34 ns for OD-CO ($2\nu_{\mathrm{OD}}$) prior to decay via inelastic scattering or chemical reaction. This is significantly longer than the laser-limited lifetime of $\leq$ 5 ns observed for OH-CO ($2\nu_{\mathrm{OH}}$), and is attributed to the closing of a near resonant vibrational energy transfer channel upon deuteration. Intermolecular bending excitation, which drives the structural transformation from the reactant complex to the transition state for reaction, results in a dramatic shortening of the lifetime to $\leq$ 5 ns. Excitation of the D-atom bend also supplies sufficient energy to reopen the near resonant vibrational energy transfer channel. Finally, an OD-CO binding energy of $D_0 \leq 500$ cm^{-1} has been established from the OD (v=1) product state distribution observed following infrared overtone excitation.

[a]On sabbatical leave from Department of Chemistry, Mount Holyoke College, South Hadley, Massachusetts 01075-6407