MAPPING THE OH + CO → HOCO REACTION PATHWAY THROUGH INFRARED SPECTROSCOPY OF THE OH-CO REACTANT COMPLEX

BETHANY V. POND, MARK D. MARSHALL,[a] and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323*.

A hydrogen-bonded OH-CO complex has been identified along the reaction coordinate for the OH + CO ↔ HOCO → H + CO_2 reaction. The vibrational spectrum of the OH-CO complex has been examined in the OH overtone region at 1.4 μm using infrared action spectroscopy, which relies on detection of OH (v = 1) fragments from vibrational predissociation by laser-induced fluorescence. The observed infrared spectrum of OH-CO consists of the pure OH overtone band at 6941.7 cm^{-1} and combination bands involving the simultaneous excitation of OH stretch and intermolecular vibrations, which appear 50 to 250 cm^{-1} higher in energy than the pure overtone. The rotational structure of the pure overtone band is indicative of a parallel transition of a linear OH-CO complex having a P = 3/2 projection of the total angular momentum on the intermolecular axis, which arises from the unquenched electronic angular momentum of OH. The OH-CO binding energy, $D_0 \leq 430$ cm^{-1}, is also established from the quantum state distribution of the OH fragments following pure overtone excitation. The strongest combination bands with 51.1, 57.1, and 247.3 cm^{-1} of intermolecular energy are attributed to geared bend and H-atom bend excitation, which are the modes that drive the transformation from OH-CO to HOCO. These combination bands exhibit rotational structures that are characteristic of perpendicular transitions ($\Delta P = \pm 1$) to states with vibrational angular momentum from the bending motions of the complex. A complete analysis of the experimental results promises to yield a spectroscopic quality characterization of the OH + CO → HOCO reaction pathway.

[a]Permanant address: Department of Chemistry, Amherst College, Amherst, MA 01002-5000