SPECTROSCOPY AND DYNAMICS OF THE HOCO RADICAL

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The HOCO radical plays a crucial role as the intermediate in the reaction of OH + CO $\rightarrow$ H + $CO_2$, yet significant questions regarding its detailed dynamics remain. Through photoelectron and photoelectron-photofragment coincidence spectroscopy on cold $HOCO^-$ and $DOCO^-$ anions, we have gained new insight into the dynamics of the strongly bound HOCO system. Photoelectron spectra probing the lower region of the deep HOCO well reveal structured spectra that are supported by Franck-Condon simulations, and allow for the reassignment of the electron affinities for both *cis*- and *trans*- isomers. Higher in the well, where tunneling from HOCO to H + $CO_2$ becomes relevant, energy-resolved tunneling lifetimes are inverted to obtain a model barrier to formation of H + $CO_2$ that is consistent with experimental internal energy distributions. Tunneling lifetimes at the top of the barrier indicate that tunneling can play an important role in this elementary reaction.

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