

Theoretical Studies of $\text{HOCO} \rightarrow \text{H} + \text{CO}_2$

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Recent experimental studies¹ by the Continetti group have concluded that the barrier between HOCO and the dissociated products $\text{H} + \text{CO}_2$ is considerably narrower than that represented in previously available potential energy surfaces (PESs).² We report here a new global PES for the HOCO system as well as additional electronic structure calculations along a minimum energy path (MEP) of the title reaction channel and initial calculations of the decay of bound HOCO through the barrier to products $\text{H} + \text{CO}_2$.

The highest level electronic structure calculations are focused on the reaction path. Calculations at the full-valence MRCI(+Q)/CBS level produce excellent agreement with known thermochemistry. Fortuitously close agreement is also obtained with the much more affordable CASPT2/avdz method using the more restrictive (13e,11o) active space. Harmonic frequencies were computed along the MEP in addition to a cubic force field expanded at the TS.

At the UCCSD(T)-F12b/AVTZ level of electronic structure calculations, a global PES has been developed Guo and coworkers.³ It also shows a significantly narrower barrier than previous PESs.

The reaction path is used to calculate the rate of decay of cis-HOCO through tunneling by a variety of methods as found in POLYRATE⁴ and as recently developed by the Barker-Stanton groups.⁵ Both canonical and microcanonical rate constants have been computed using these two approaches and significant tunneling has been found. In addition, the H/D kinetic isotope effects have been obtained. Results will be contrasted with the experimental studies.

References

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