Tunneling Facilitated Dissociation to H+CO_{2} in HOCO^{-} Photodetachment

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Dissociative photodetachment of HOCO$^-$ is investigated with both five and six-dimensional quantum models on an *ab initio* based accurate potential energy surface. Three experimentally observed channels, namely HOCO, H + CO$_2$, and HO + CO, were identified in our theoretical simulations. Since the energy spectrum of the initial HOCO species prepared by photodetachment is mostly lower than both the HO + CO asymptote and dissociation barrier to H + CO$_2$, the production of H + CO$_2$ is almost exclusively *via* tunneling. However, the lowest-lying HOCO resonances are extremely long lived (~µs), which might elude experimental measurements through its decay products H + CO$_2$. Our results are in good agreement with almost all experimental data reported by the Continetti group using a new cryogenically cooled photoelectron-photofragment coincidence apparatus.

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Photodetachment of negative ions has been widely used as a powerful tool to probe dynamics of chemical reactions on potential energy surfaces (PESs) of the corresponding neutral species.[1] A distinct advantage of this approach is the direct access to the transition-state region of the bimolecular reactions. The so-called transition-state spectroscopy by negative ion photodetachment has revealed intricate quantization near the reaction barrier,[2] which often controls the reactivity. In this Letter, we focus on the dynamics of dissociative photodetachment of the HOCO[-] anion, which allows the preparation of the neutral HOCO species above and below its dissociation bottlenecks for both the HO + CO and H + CO_2 channels. By accessing both the reaction intermediate and a dominant transition state, such studies provide a unique perspective to the HO + CO → H + CO_2 reaction, which is considered to be the "second most important combustion reaction"[3] and serves as a tetratomic prototype for complex-forming reactions.[4-5] In addition, they offer a stringent accuracy test of the relevant PESs.

The PES governing both the HO + CO → H + CO_2 reaction and the dissociative photodetachment of HOCO[-] is schematically shown in Fig. 1.[6-9] Despite its large exothermicity, the bimolecular reaction proceeds *via* a complex-forming mechanism, involving both the trans and cis-HOCO species as reaction intermediates.[10-11] It is clear from this figure that the reaction has bottlenecks in both the entrance channel (TS1) and exit channel (TS2), which are responsible for its well-known non-Arrhenius kinetics.[12-13] One of key issues concerning the kinetics and dynamics of this important reaction is the possible tunneling under TS2, characterized by an imaginary frequency dominated by the H-O stretch. Circumstantial evidence for tunneling includes a strong OH/OD kinetic isotope effect[12] and enhanced reactivity by OH vibrational excitation.[14]

The photodetachment of HOCO[-] (and DOCO[-]) has been extensively investigated by Continetti and his coworkers.[15-20] The ejection of an electron from the anion places the system on the neutral PES. Earlier photoelectron-photofragment coincidence (PPC) experiments revealed the formation of the HOCO, HO + CO, and H + CO_2 products.[15-16] More recently, a new cryogenically cooled PPC apparatus was used to eliminate hot bands and to achieve much higher resolution.[18-19] One of most striking observations is that nearly all photoelectrons in the H + CO_2 channel were found to have energies above the maximum limit predicted for TS2, suggesting most dissociation of HOCO into the H + CO_2 channel is *via* tunneling through the barrier.[18-19] In

other words, the reaction is pure quantum mechanical in nature. While tunneling represents a well-known quantum phenomenon in molecular systems, chemical reactions dominated by deep tunneling are uncommon. In two examples found recently,[21-22] for example, the dominant products are produced *via* deep tunneling over a higher barrier even when another channel with a lower barrier is available. These unique reaction systems, along with the one reported here, suggest that quantum mechanical effects such as tunneling can in many cases dominate, rather than merely influence, reactive systems.

Obviously, a correct account of tunneling has to resort to quantum mechanics. To this end, the photodetachment of HOCO⁻ has been studied quantum mechanically by Zhang *et al.*[23] before. Although all three channels were identified, this earlier theoretical work found no evidence for tunneling. There are several many reasons for the discrepancy. The most likely is that the Lakin-Troya-Schatz-Harding (LTSH) PES[7] used in the calculation was not sufficiently accurate, particularly with regard to the thickness of the barrier associated with TS2, as shown in our recent work.[9] As a result, tunneling might be substantially underestimated. Indeed, our own calculations using the same five-dimensional model described below found only negligible tunneling on the LTSH PES.

In this Letter, we reinvestigate the problem using our new chemically accurate full-dimensional HOCO PES based on extensive *ab initio* calculations,[9] which has found a much thinner barrier leading to the H + CO_2 products than the LTSH PES. While the low-resolution energy spectrum of the photodetachment was computed using a full-dimensional model, we chose to describe the dynamics using a five-dimensional model with the non-reacting C-O bond fixed, in order to make sure of the inclusion of long time events due to tunneling. While recent quantum dynamical studies have shown that the non-reactive CO bond is not in the strict sense a spectator in the HO + CO reaction,[24-25] we do not believe this approximation will qualitatively change the conclusion for photodetachment, especially concerning the tunneling over TS2. This is because the C-O bond length does not change significantly over the course of the dissociation. In a future study, the full-dimensional dynamics will be studied.

Our investigation started with the development of a near-equilibrium PES for the HOCO⁻ anion. About 10000 *ab initio* points using the F12b version of the coupled-cluster singles and doubles and perturbative triples (CCSD(T)-F12b) method[26] with the AVTZ basis set were

3

calculated using MOLPRO package.[27] The six-dimensional double-well HOCO⁻ PES was obtained by fitting these points using the permutation invariant polynomial method of Bowman and coworkers,[28] in the same manner described in our recent work on the HOCO PES.[9] The cis-HOCO⁻ species is lower than the trans-HOCO⁻ species by 0.067eV, and the two isomers are separated by a barrier of 0.411 eV. The geometric parameters and energies of the two potential minima are given in Table I, along with those obtained in previous theoretical work.[15]

The dynamical calculations were carried out using the diatom-diatom Jacobi coordinates, namely ($r_1, r_2, r_3, \theta_1, \theta_1, \phi$). Here, r_1 and r_2 are the OH and CO bond lengths and r_3 is the distance between the two diatomic centers of mass, where θ_1, θ_2, and ϕ denote the polar and dihedral angles, respectively. In the five-dimensional calculations reported here, r_2 is fixed at 2.23 bohr. The total rotational angular momentum of the system is set to zero. The neutral PES was the more recent version, denoted as CCSD2/d,[29] in which some unphysical features in its predecessor (CCSD1/d)[9] have been removed.

To prepare for the initial wavefunction on the neutral PES, we have first calculated the lowest vibrational state of the cis-HOCO⁻ anion, which is expected to dominate in the low-temperature experiment.[18] The wavefunction was then placed on the neutral PES assuming a vertical Condon transition. It should be noted that the geometry of the anion is sufficiently similar to that of the corresponding neutral species, very little amplitude is found outside the HOCO wells on the neutral PES. The wave packet was then propagated using the Chebyshev propagator[5] associated with the neutral state Hamiltonian. The cosine Fourier transform of the autocorrelation function yields the energy spectrum.[30] The positions and widths of tunneling resonances in the HOCO wells were then estimated using filter-diagonalization.[31] In addition, the dissociation probabilities into both the HO + CO and H + CO₂ channels were computed using a flux method, in which the corresponding dividing surfaces are placed at r_1 = 3.25 bohr and r_3 = 4.67 bohr.

The low-resolution energy spectrum for the photodetachment of HOCO⁻ is displayed in Fig. 1 for both the full and five-dimensional models. These spectra were obtained from the Fourier transform of the corresponding autocorrelation functions after a short (100 steps) propagation of the initial wave packets on the neutral PES. In the same figure, we have also included the

spectrum converted from the experimental electronic kinetic energy (eKE) distribution[18] *via* the following relation: $E = h\nu - eKE$, where the experimental photon energy is 3.21 eV (386 nm).[18] The agreement between the experimental distribution and the full-dimensional spectrum is excellent, validating the PESs used in the calculations. The shift of the reduced-dimensional spectrum can be attributed to the freezing the non-reactive CO bond.

Interestingly, we note that the energy spectrum is mostly lower than both the HO + CO asymptote and the TS2 barrier. This observation is important because it indicates that only a small fraction of the neutral species will dissociate directly into both the HO + CO and H + CO_2 channels. On the other hand, the majority of the neutral species prepared by photodetachment is temporarily trapped in the HOCO well as metastable resonances, as discussed below, and has no choice but to decay *via* tunneling through the barrier under TS2.

To illustrate this point, a higher resolution energy spectrum of HOCO prepared by photodetachment of cis-HOCO⁻ is displayed in Fig. 2. The spectrum was obtained after 70,000 Chebyshev propagation steps, which correspond to a few ps in real time. As expected, all HOCO species below the effective dissociation barriers exist as resonances, which are the sharp peaks in the figure. There is no bound state because the lowest-lying vibrational state of cis-HOCO is above the H + CO_2 asymptote. Based on inspection of wavefunctions, these peaks can be assigned to bending (ν_5) progressions, due apparently to the fact that the bending angles of the anion differ significantly from those of the neutral species. Some excitation in the reactive C-O bond stretch (ν_4) is also present. On the other hand, the OH bond length in the negative ion and the neutral species is roughly the same, resulting in negligible excitation. This assignment is in good agreement with the most recent photoelectron spectroscopic study of the cold HOCO⁻ anion, in which bending progressions in ν_5 with some excitations in ν_4 and ν_3 (HOC bend) were found.[20] As discussed in our recent work,[29] the vibrational frequencies of both cis and trans-HOCO species calculated on our PES are in good agreement with these experimental results as well the high-level *ab initio* data reported in the same publication.[20]

The widths of these resonances have been estimated and they are grouped in Fig. 2 based on their calculated lifetimes. It is clear that some of the resonances have exceedingly long lifetimes (>µs), which are comparable to the flight time in the experimental set up.[19] As a result, these resonances would have been classified as stable HOCO species in the experiment. Close to the energy of TS2, the lifetimes are on the order of ps, which can be readily captured in our flux

calculations as discussed below. The range of the lifetimes reported here are consistent with the estimates based on an earlier effective one-dimensional model.[19] Above the dissociation limit, there are still resonances superimposed on broad features, which correspond to direct dissociation.

The calculated dissociation probabilities to the HO + CO and H + CO_2 channels are shown in Fig. 3, as well as in Fig. 1. These results were obtained from flux calculations with 70,000 Chebyshev steps, thus corresponding to a few ps. In the HO + CO channel, the energy distribution centers at 1.82 eV relative to the trans-HOCO global minimum, in good agreement with the experimental distribution between 1.65 and 2.0 eV.[18] Comparing with the H + CO_2 channel, the HO + CO fraction is substantially smaller, again consistent with experiment.[18] On the other hand, the probability for the H + CO_2 channel has contributions from both above and under the TS2 barrier. The former converges quickly because of the relatively short time needed to dissociate. However, the tunneling contribution, which is apparent in the figure below the dissociation limit, is not quite converged in our calculation due to the extremely long lifetimes of the resonances at low energies. Nonetheless, it is clear that the tunneling channel makes up a large percentage of the total photodetachment.

In comparing with the experimental branching ratios, it is important to realize that the experimentally detected HOCO species are not stable because these resonances have energies higher than the dissociation asymptote. However, lifetimes of these deep tunneling states are so long that the 7.8 μs flight time[19] might still be insufficient to observe their decomposition. As discussed above, it is impractical to expect wave packet propagations on such time scales either. Consequently, there is substantial uncertainty in the partition of the HOCO and H + CO_2 channels below the barrier. However, this uncertainty does not affect the overall agreement between theory and experiment. The calculation results presented here clearly demonstrated that photodetachment of HOCO⁻ produces predominantly HOCO resonances that dissociate into H + CO_2, in agreement with the conclusion made by Continetti and coworkers.[19]

To summarize, we report here a quantum mechanical characterization of the dissociative photodetachment of HOCO⁻, using accurate PESs for both the neutral and anion species. In good agreement with experiment, the results indicate the production of all three experimentally observed channels, namely HO + CO, H + CO_2, and HOCO. Progressions of HOCO vibrational states have been found and their intensities are in good agreement with the recent photoelectric

spectra of the cold HOCO⁻ anion. More importantly, the quantum calculations confirm the experimental observation that the production of H + CO_2 is primarily *via* tunneling, with some low-lying resonance decay with μs lifetimes. The good agreement with the PPC experiment provides strong evidence for the accuracy of the new PES. It also highlights the ability of theory to provide quantitatively accurate interpretations of experimental observations.

Table I. Geometry parameters (in Å and degrees) and energies (in eV) of the cis and trans-HOCO⁻ minima. The six geometry parameters are the internal coordinates with O′ initially bonded to C of CO′.

Species	level	R_{HO}	R_{CO}	$R_{CO'}$	θ_{HOC}	$\theta_{OCO'}$	$_{HOCO'}$	E	ZPE
t-HOCO⁻	CCSD(T) [a]	0.961	1.506	1.214	100.3	110.8	180.0	-1.233	0.497
	This work	0.9609	1.5063	1.2122	100.620	110.770	180.0	-1.309	0.513
c-HOCO⁻	CCSD(T) [a]	0.977	1.450	1.231	102.2	111.9	0.0	-1.303	0.512
	This work	0.9774	1.4490	1.2300	102.472	111.832	0.000	-1.376	0.512

a. CCSD(T)/6-311++G(3df, 3pd).[15]

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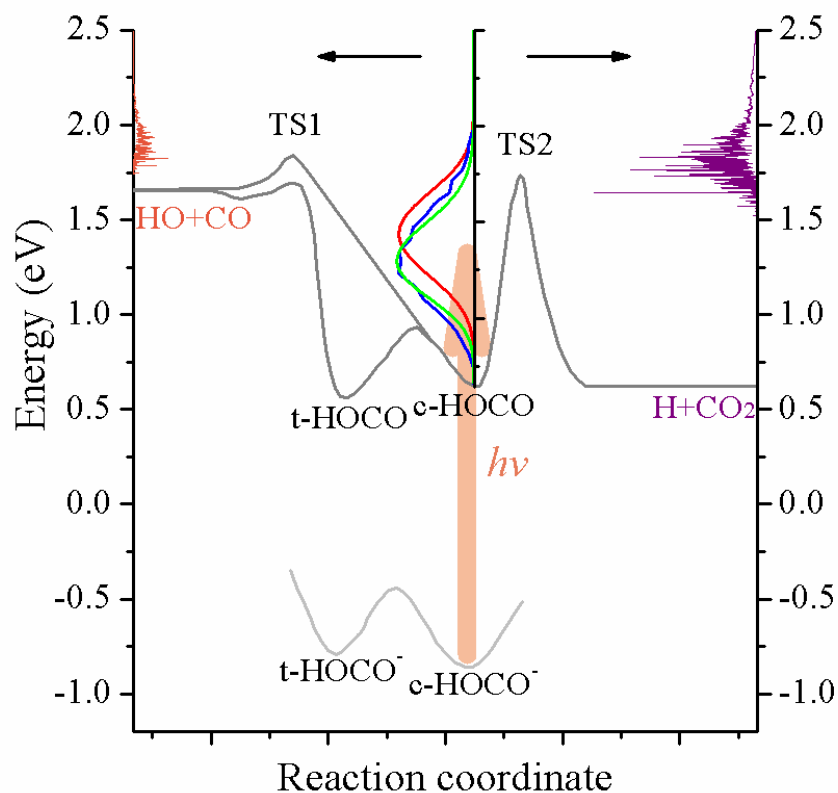31 H. Guo, Rev. Comput. Chem. **25**, 285 (2007).

Figure 1. Zero-point corrected energetics of the schematic HOCO/HOCO⁻ PESs. The energy zero is placed at the global trans-HOCO minimum of the neutral PES. The calculated energy spectrum of the HOCO species prepared by photodetachment of the HOCO⁻ anion is displayed in green (full-dimensional model) and red (five-dimensional model) with the experimentally derived spectrum in blue. In addition, the calculated dissociation probabilities for the HO + CO and H + CO_2 channels are also given in orange and purple. Note the substantial probabilities in the latter channel suggest tunneling.
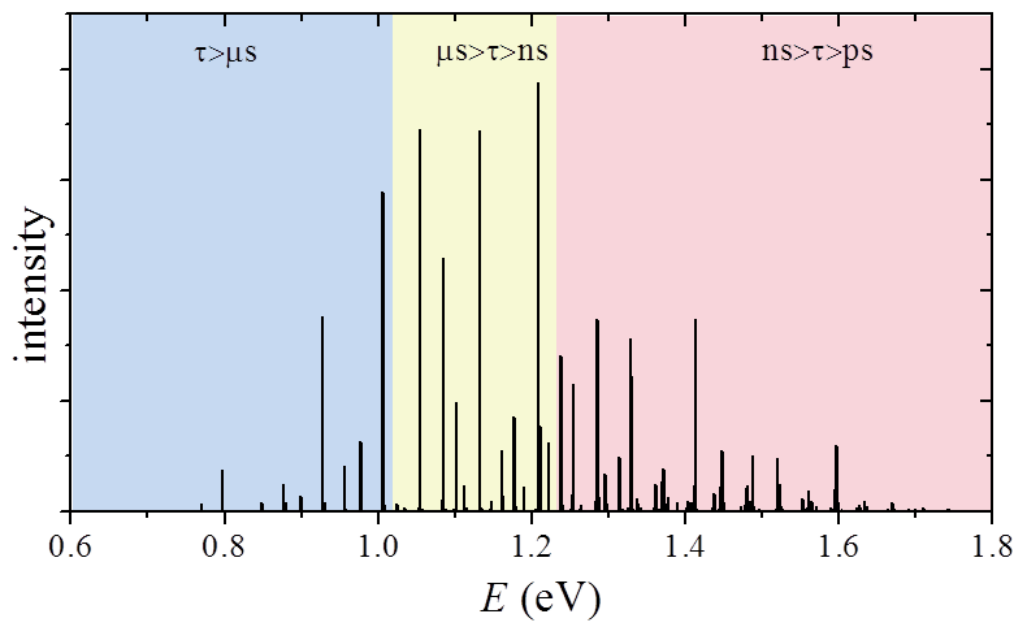
Figure 2. High-resolution energy spectrum for HOCO prepared by photodetachment of the HOCO⁻ anion. The energy is referenced to the trans-HOCO potential minimum and the approximate lifetime ranges of the resonances are color coded in blue for µs; orange for ns, and red for ps.
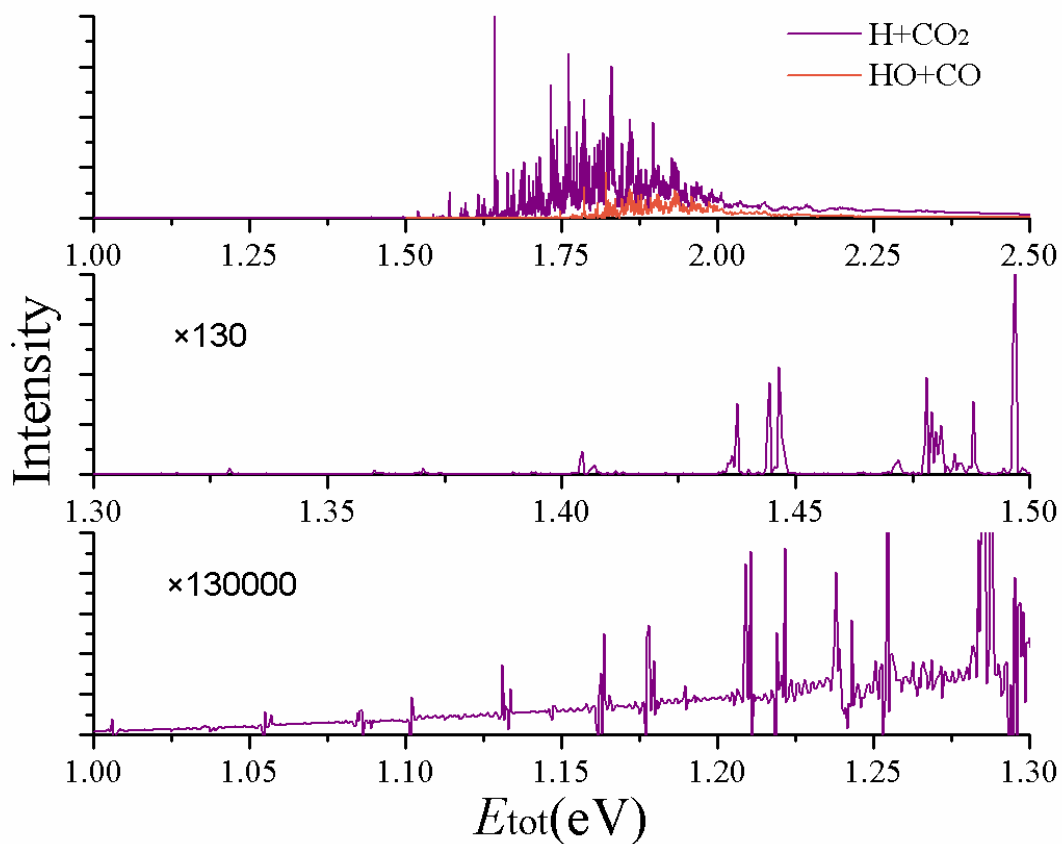
Figure 3. Dissociation probabilities for the HO + CO (orange) and H + CO$_2$ (purple) channels, respectively. The lower energy signals are amplified by 130 and 130000 times respectively in the middle and lower panels. The tunneling is evident for the H + CO$_2$ channel at energies lower than TS2 (1.73 eV).