Communication: New insight into the barrier governing CO2 formation from OH + CO

Christopher J. Johnson
University Of California

Berwyck L. Poad
University of Wollongong, bpoad@uow.edu.au

Ben B. Shen
University Of California

Robert E. Continetti
University Of California

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Communication: New insight into the barrier governing CO2 formation from OH + CO

Abstract
Despite its relative simplicity, the role of tunneling in the reaction OH + CO → H + CO(2) has eluded the quantitative predictive powers of theoretical reaction dynamics. In this study a one-dimensional effective barrier to the formation of H + CO(2) from the HOCO intermediate is directly extracted from dissociative photodetachment experiments on HOCO and DOCO. Comparison of this barrier to a computed minimum-energy barrier shows that tunneling deviates significantly from the calculated minimum-energy pathway, predicting product internal energy distributions that match those found in the experiment and tunneling lifetimes short enough to contribute significantly to the overall reaction. This barrier can be of direct use in kinetic and statistical models and aid in the further refinement of the potential energy surface and reaction dynamics calculations for this system.

Keywords
barrier, into, formation, governing, oh, insight, co, communication, co2, GeoQUEST

Disciplines
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Communication: New insight into the barrier governing CO$_2$ formation from OH + CO

Christopher J. Johnson,$^1$ Berwyck L. J. Poad,$^2$ Ben B. Shen,$^2$ and Robert E. Continetti$^{2,a}$

$^1$Department of Physics, University of California San Diego, 9500 Gilman Dr., La Jolla, California 92093-0354, USA
$^2$Department of Chemistry and Biochemistry, University of California San Diego, 9500 Gilman Dr., La Jolla, California 92093-0340, USA

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Despite its relative simplicity, the role of tunneling in the reaction OH + CO → H + CO$_2$ has eluded the quantitative predictive powers of theoretical reaction dynamics. In this study a one-dimensional effective barrier to the formation of H + CO$_2$ from the HOCO intermediate is directly extracted from dissociative photodetachment experiments on HOCO and DOCO. Comparison of this barrier to a computed minimum-energy barrier shows that tunneling deviates significantly from the calculated minimum-energy pathway, predicting product internal energy distributions that match those found in the experiment and tunneling lifetimes short enough to contribute significantly to the overall reaction. This barrier can be of direct use in kinetic and statistical models and aid in the further refinement of the potential energy surface and reaction dynamics calculations for this system. © 2011 American Institute of Physics. [doi:10.1063/1.3589860]

The elementary reaction OH + CO → H + CO$_2$ has been the subject of extensive theoretical and experimental studies, yet the detailed dynamics remain poorly understood. This reaction governs CO/CO$_2$ ratios in hydrocarbon combustion and the upper atmosphere, and impacts the OH$_x$/NO$_x$/SO$_x$ atmospheric cycles through the destruction of OH radicals.\(^1\) It is one of the simplest complex-forming elementary reactions; it is strongly exothermic but features a very stable intermediate, HOCO, and a barrier to activation in the product channel of roughly similar energy to the reactants.\(^2-4\) As a four-atom system, the OH + CO → HOCO → H + CO$_2$ reaction is amenable to a broad range of theoretical treatments,\(^2,5-8\) and several high-level potential energy surfaces (PES) exist.\(^9-13\) The reaction proceeds through the strongly bound cis-HOCO intermediate\(^14\) and shows striking non-Arrhenius behavior.\(^9\) The exact height and shape of the barrier to the formation of H + CO$_2$ are critical to the overall kinetics of the reaction. However, beyond limited spectroscopic studies\(^15-21\) and measurements of excited state dynamics,\(^22\) little experimental information exists on the isolated HOCO radical, and there is no quantitative agreement on the nature of the barrier and the role that tunneling plays in the overall kinetics of the OH + CO reaction.\(^9,23-25\)

Photoelectron-photofragment coincidence (PPC) spectroscopy\(^26\) has been used to directly probe the HOCO PES governing the dynamics of this reaction, resolving three processes: detachment to internally excited HOCO radicals (stable channel), dissociation to H + CO$_2$ (exit channel), and dissociation to OH + CO (entrance channel).\(^27,28\) All dissociation to H + CO$_2$ was found to occur below the calculated barrier on the neutral PES, consistent with tunneling dissociation. Further analysis revealed dissociation to OH + CO with lifetimes less than 9 × 10$^{-13}$ s, indicating that when energetically allowed, this process is facile.\(^29\) However, these results were complicated by the presence of strong hot bands evident in the photoelectron spectra. Recent incorporation of a cryogenic electrostatic ion beam trap, providing internally cold anions, allowed for unprecedented insight into these dynamics, confirming the occurrence of tunneling through the exit-channel barrier.\(^30\) Energy-resolved branching fractions were measured for the three processes, revealing a range of internal energy in which tunneling lifetimes to H + CO$_2$ are similar to the timescale of the experiment indicative of competition between the stable and exit channels. In the present work these studies are extended to the deuterated DOCO radical\(^31\) and the set of energy-resolved branching fractions are analyzed in detail in the tunneling regime, enabling the development and optimization of a realistic one-dimensional (1D) potential barrier that accurately reproduces the observed tunneling dynamics and independently predicts the observed product internal energy distributions.

The PPC spectra for HOCO\(^-\) (DOCO\(^-\)) + h\(_\nu\) → H(D) + CO$_2$ + e\(^-\) in Fig. 1 provide the primary evidence for the presence of tunneling in the exit channel. All dissociation to H + CO$_2$ occurs above the maximum electron kinetic energy (eKE) limit denoted by horizontal lines and, barring significant errors in the computed surfaces, is therefore due entirely to tunneling. However, an interesting horizontal feature is present in both spectra at the high eKE (low energy on the PES) limit. In dissociative systems PPC spectra generally exhibit diagonal features due to the correlation of energy in the system to energy along the dissociative coordinate. The transition from diagonal to horizontal character at the high eKE limit of both spectra indicates that the tunneling lifetime approaches the time-of-flight (TOF) of the translational spectrometer, 7.8 $\mu$s for HOCO and 7.9 $\mu$s for DOCO, at these energies. If a metastable HOCO\(^*\) neutral travels a significant
portion of the TOF before dissociating, the measured translational energy release (ET) is reduced, and thus a discrete ET is mapped into a band of apparent ET extending from the actual value to zero. This horizontal feature appears at lower eKE (higher E_{int}) in the DOCO spectrum as expected due to the reduction in tunneling probability from the larger reduced mass of D + CO$_2$. The spectra are also shifted below the maximum total energy release (diagonal lines), indicating that 0.1–0.4 eV of the available energy is stored as internal energy in the CO$_2$ product.

Energy-resolved branching fractions are determined from the relative contribution of each product channel at a given energy to the overall photoelectron spectrum. In the region of competition between the stable channel and the exit channel, the stable fraction can be used to compute tunneling probabilities. A 1D barrier to dissociation can be optimized to fit these tunneling probabilities using a quasi-1D model, simplified from one outlined by Miller. In this model nuclear motion is assumed to be separable into dissociative and non-dissociative components and dissociative motion is treated as a two-body 1D system (H-OCO). All non-dissociative internal energy resides entirely in OCO and the partitioning of this energy is controlled by an experimentally determined parameter \( \chi \), while only dissociative energy is considered for tunneling through the barrier. The experimentally derived potential is composed of a Morse oscillator coupled to a dissociative potential, and is plotted in Fig. 2 along with a fully relaxed, zero-point corrected scan of the energy along the OH bond length using the CCSD/aug-cc-pVTZ level of theory.

Comparison of the experimental barrier with the computed minimum-energy barrier shows good agreement for the bound part of the surface and distinct differences for the dissociative part. The curvature parameter of the Morse potential gives an OH stretching frequency of 3486 cm$^{-1}$, in good agreement with the computed value. The zero-point corrected barrier height is found to be 1.13 eV at 1.44 Å, displaced to larger \( r_{OH} \) by 0.09 Å and 0.02 eV higher than the minimum-energy barrier but significantly wider. Among the available full PESs, ZPE-corrected saddle points range from 0.97 to 1.28 eV, consistent with the model barrier.

The computed minimum energy barrier is not expected to properly reproduce the tunneling dynamics in the HOCO system. Calculations show significant geometrical changes as the system crosses the barrier, particularly in the OCO angle, which changes by nearly 40° over a 0.05 Å change in \( r_{OH} \). Thus, relaxed scans along \( r_{OH} \) reflect these geometrical changes and represent a lower limit, at each bond length, to

FIG. 2. Model PES for cis-HOCO → H + CO$_2$, shown in black, and calculated minimum-energy barrier (green crosses). Also included are the relevant OH (blue) and OD (red) vibrational levels and the range of \( E_{int} \), where long-lifetime tunneling is observed for each isotopologue. An example of expected product internal energy, given by \( E_{int, prod} \), is also shown.
the barrier through which tunneling occurs. Since H atom
tunneling occurs rapidly compared to the motion of OCO, tun-
neling must occur at essentially constant CO₂ geometry,
and therefore is nearly perpendicular to the minimum-energy
pathway in the relevant (r₀H, ∠OCO) plane of the surface, ex-
emplified in Fig. 3.

Using the model barrier the internal energy in the CO₂
products resulting from tunneling can be estimated and com-
pared to the experimental values. Significant vibrational exi-
citation in the CO₂ product is expected due to the difference be-
tween the tunneling geometry and the equilibrium CO₂ geom-
etry. Thus, the energy at the outer limit of the tunneling path
gives an estimate of the internal energy in the CO₂ fragment.
The difference between the calculated and experimentally de-

erived barriers in the repulsive region is ~0.2–0.3 eV, arising
from the un-relaxed nature of the OCO fragment during tun-
neling. Comparison of this expectation with the average internal
energy from the coincidence spectra of 0.2 eV for HOCO
and 0.3 eV for DOCO shows close agreement. A second in-
dependent confirmation involves the energy partitioning factor χ
relating total internal energy to internal energy in the
bond-breaking coordinate. While the quasi-1D model implicit-
ly requires vibrational adiabaticity, this is not enforced in the

extraction procedure. This implies that the CO₂ fragment in-
ternal energy, once dissociation is complete, should equal the
non-dissociative energy component, E_{int} - E_{diss}, which also
ranges from 0.1 to 0.3 eV. The agreement of both of these
checks without inclusion of experimental information regard-
ing the product internal energy provides strong evidence that
the model captures most of the important dynamical aspects
of the system. The slight discrepancy in the internal energy
distribution ranges from the model indicate that vibrational
adiabaticity does not strictly hold, with partitioning of energy
between kinetic and internal degrees of freedom as the OCO
equilibrium geometry relaxes suddenly from bent to linear in
the exit channel.

While the model potential is able to reproduce the exper-
imental tunneling rates extremely well, tunneling lifetimes
become too short relative to the time-scale of the measure-
ment to determine the fraction of stable radicals near the top
of the barrier. Given the 1D approximation used here, the
possibility that the actual barrier and tunneling rates deviate
from the model at the top of the barrier cannot be ruled out.
As the tunneling distance approaches zero the tunneling path-
way must approach the minimum energy pathway implying
that the extracted barrier shape should approach the shape of
the minimum-energy barrier at the saddle-point. The failure
to do so could indicate inapplicability of the barrier at these
energies, dynamics beyond those explicitly considered in the
model, or that the minimum-energy barrier fails to capture
the tunneling dynamics at any energy. However, the veracity
of the model barrier is supported by the observation in Fig. 3
that the tunneling pathway and the minimum-energy pathway
intersect near the saddle point, implying little geometric
change as a function of energy for this plane of the PES.

Tunneling lifetimes are computed using the model bar-
rier over its full energy range, shown in Fig. 4 as a function
of energy in the dissociation coordinate. It can be seen that in
the particularly relevant region near the entrance channel en-
ergy of 1.2 eV, the tunneling lifetimes are predicted to be less
than 1 psec, similar to the measured lifetime of the HOCO
→ OH + CO process, implying that slight collisional sta-
bilization or temporarily bound complexes could lead to non-
negligible dissociation through this barrier. Even above the
barrier, where dissociation is expected to be facile, frustration
due to curvature of the reaction path may also cause tunnel-
ing above and away from the saddle point energy to become
competitive. Tunneling rates for the minimum energy bar-
rier, also in Fig. 4, give a lower limit to the tunneling life-
times and thus can be used in concert with the model lifetimes

FIG. 3. An example 2D slice (r₀H, ∠OCO) at fixed r₀C = r₀O = 1.18 Å of the
HOCO PES (non-ZP corrected). The computed minimum energy path (solid)
is overlaid and the path of highest tunneling probability (dashed) is shown for
an example value of E_{diss}.

FIG. 4. Prediction of tunneling lifetimes as a function of energy in the OH
(red) and OD (blue) stretch (solid lines) compared to those taken from the
theoretically predicted minimum energy barrier (dashed).
to constrain the rates of processes occurring in this energy regime of the PES.

The data presented here can be of direct use in more sophisticated treatments of the tunneling process\textsuperscript{34–36} particularly with regard to the role of vibrational energy distribution in the HOCO\textsuperscript{*} intermediate which is treated crudely in this model. Additionally, the effect of isomerization to trans-HOCO acting as a sink for cis-HOCO\textsuperscript{*} that would otherwise tunnel is not considered. If this process occurs, the actual tunneling rates could be significantly higher than those predicted by the model barrier. The lowest-energy transition state between cis- and trans-HOCO is reached by out-of-plane torsional motion of the H atom. Excitation of the torsional mode of HOCO is not expected in photodetachment due to the planarity of both the anion and the neutral and inefficient vibrational redistribution due to the $\Sigma^\mathrm{a}$ symmetry of the torsional mode, so this transition state should be inactive as a mechanism for the loss of cis-HOCO\textsuperscript{*}. However, a poorly characterized higher energy planar isomerization transition state also exists which could result in a reduction in the actual tunneling yield if it is found to have low enough energy. Work on a more detailed transition-state-theory model of the global kinetics on this surface which can accurately reproduce these dissociative photodetachment results should help to further illuminate the role that tunneling plays in the overall dynamics of this reaction.

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