An experimental study of the dissociative photodetachment (DPD) dynamics of HOCO$^-$ and DOCO$^-$ at a photon energy of 3.21 eV has been carried out to probe the potential energy surface of the HOCO free radical and the dynamics of the OH+CO$\rightarrow$H+CO$_2$ reaction. These photoelectron-photofragment coincidence experiments allow the identification of photodetachment processes leading to the production of stable HOCO free radicals and both the H+CO$_2$ and OH+CO dissociation channels on the neutral surface. Isotopic substitution by deuterium in the parent ion is observed to reduce the product branching ratio for the D+CO$_2$ channel, consistent with tunneling playing a role in this dissociation pathway. Other isotope effects on the detailed partitioning of kinetic energy between photoelectrons and photofragments are also discussed. The results are compared to recent theoretical predictions of this DPD process, and evidence for the involvement of vibrationally excited HOCO$^-$ anions is discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731787]
involves trans-HOCO converting to the C2v symmetry H-·CO2 conformer over a high barrier (TS4) with subsequent dissociation into H+CO2.6,16,32–39 The OH+CO reacting system has been observed in cryogenic matrices19–21 and the gas phase,22–29 and their rotational23–28 and vibrational frequencies19–21 have been reported and can be directly compared with calculated values. Lester and co-workers reported spectroscopic evidence for the OH··CO complex in the OH+CO entrance channel.18,30,31 Additionally, significant experimental and theoretical efforts have been carried out to study the pressure and temperature dependences of the rate coefficient of the OH+CO reaction, providing evidence for a deep HOCO well and a high barrier leading to the formation of H+CO2.34–39 The OH+CO (Refs. 40–43) and H+CO2 (Refs. 44–48) collisions have been studied by various experimental techniques as well, yielding cross sections and internal energy distributions in reaction products. These experimental results can be compared with theoretical predictions based on ab initio PESs and classical/quasiclassical trajectory theories8,9,11,17,49,50 or quantum dynamics calculations49–56.

However, there remains a lack of detailed and direct measurement of the global HOCO PES. For instance, it is difficult to measure the depth of the HOCO potential well accurately. Early attempts were made to obtain a heat of formation of the HOCO radical by measuring the appearance potential of C2H2+ from electron impact of C2H2CO2H or CH3C=C=O from CH3CO2H.57,58 reporting ΔfH0 to be −39 and −58±4 kcal/mol, respectively. Ruscic et al. obtained ΔfH0 = −52.5±0.6 kcal/mol directly by the photoionization of the HOCO radical.22 Later this value was revised to be ΔfH0
the more stable formate anion, HCO$_2^-$ flowing afterglow experiments studying the hydroxide-

0.02 eV for the

not available in the recent work of Dixon and co-workers. In

an accurate prediction for the AEA of the

trans-

Schatz, and Harding

different studies, and a direct measurement of the

height of the various transition states on this PES has yet to be completed.

Recently the dynamics and PES of the HOCO free radical were studied by Clements et al. using DPD of the anion precursor HOCO$^-$.

Using photoelectron-photofragment co-

cal were studied by Clements of the two HOCO isomers

HOCO$^-$ + H + CO$_2$ + e$^-$.

While the majority of photodetachment products are stable HOCO radicals, unimolecular dissociation into H+CO$_3$ and OH+CO fragments, as well as the evidence for direct DPD on a repulsive excited electronic state yielding ground state OH+CO+e$^-$, were observed.

The DPD studies are based on the discovery and character-

ization of a stable, bound HOCO$^-$ anion precursor. The first experimental evidence for this species was reported in flowing afterglow experiments studying the hydroxide-transfer reaction of H$_2$O$^+$+CO and indicated the presence of a negative ion with m/e=45 that was determined not to be the more stable formate anion, HCO$_2^-$. Interpretation of the DPD experiments was aided by high-level ab initio calculations on HOCO$^-$ and HOCO by Clements et al.

The adiabatic electron affinities (AEAs) of the two HOCO isomers were predicted to be 1.43 eV (cis) and 1.30 eV (trans), respectively from CASSD(T) calculations [Clements, Continetti, and Francisco (CCF), see Table I], which agrees well with the DPD measurements.

The same calculation predicted a deeper neutral HOCO well compared with most of the other calculations listed in Table I, except for the Lakin, Troya, Sacht, and Harding (LTSH) results. Dixon et al. recently predicted an AEA for trans-HOCO of 1.36 eV as well as the energy of the cis anion [see Dixon, Feller, and Francisco (DFF) results in Table I]. These authors reported the energetics of both cis- and trans-HOCO radicals using a slightly different theoretical approach elsewhere [see Feller, Dixon, and Francisco (DFD) results in Table I], with a 0.02 eV difference seen between the depth of the trans-HOCO well reported in the DFF (Ref. 62) and FDF results. Therefore, an accurate prediction for the AEA of the cis conformer is not available in the recent work of Dixon and co-workers.

In addition, the anion stability relative to the OH+CO asymptote predicted by CCF and DFF only differs by 0.03 and 0.02 eV for the trans- and cis-HOCO$^-$ isomers, respectively (see Table I). Thus, we will continue to use the consistent level of theory for both anions and neutrals reported by CCF.

The previous DPD study provided important experimental information on the HOCO PES. However, there are several questions remaining unanswered, in particular, the role played by tunneling in the dissociation to H+CO$_2$, the observation of a significant fraction of the OH+CO+e$^-$ products at total kinetic energies beyond the calculated energetic maximum, and a detailed comparison of the product branching ratios with statistical and quantum dynamical predictions. To achieve a better understanding of the reaction mechanisms and energetics of this system, in the current work we compare the DPD dynamics of the deuteronated anion DOCO$^-$ with HOCO$^-$ at a photodetachment wavelength of 386 nm ($E_{ph}=3.21$ eV). The use of a longer wavelength in this study removes potential contributions from excited electronic states of HOCO and provides improved photoelectron kinetic energy resolution. Following a brief review of the experimental technique, the photoelectron spectra corresponding to channel (1) and the PPC spectra arising from the DPD channels (2) and (3) for both isotopologs will be presented, as well as the branching ratios for the three neutral product channels. The observed isotope effects and inferred DPD mechanisms will be discussed in detail and compared with recent theoretical predictions by Zhang et al.

II. EXPERIMENT

The fast-ion-beam PPC spectrometer employed in the present study is capable of measuring angle-resolved photoelectron and photofragment kinetic energies from a single DPD event in coincidence, allowing a direct probe of the dissociation dynamics on the neutral PES after photodetachment. The experimental approach is similar to the previous DPD study by Clements et al. with the exception that a new multiparticle photofragment imaging detector was used in this study and the photoelectron spectra were solely recorded by an imaging detector. Therefore only a brief review of experimental method will be presented here. In the final measurements reported here, the HOCO$^-$ anion (m/e=45) was created using electron impact on a 1 kHz pulsed supersonic expansion of 7% CO, 6% N$_2$O, 17% CH$_4$, and 70% N$_2$. For the DOCO$^-$ experiments, CD$_4$ (99%, Cambridge Isotope Laboratory) instead of CH$_4$ was used in the precursor gas mixture. Here N$_2$ was used to dilute the gas mixture and assist the collisional cooling in supersonic expansion. An alternative experiment without N$_2$ showed no observable difference, ruling out the involvement of OH$^-$ (N$_2$) species (m/e=45) in the present study. A plausible mechanism for the generation of the HOCO$^-$ anion involves electron impact on the N$_2$O/CH$_4$ mixture forming OH$^-$ followed by the association of OH$^+$ with CO to form HOCO$^-$ in the free-jet expansion. The nozzle-skimmer distance used in these experiments was 1.5–2.0 cm, and an interesting observation was made that HOCO$^-$ was formed most effectively when the electron beam was closer to the skimmer aperture. Thus, the condensation of neutrals into clusters followed by electron impact on those clusters may play an important role in the production of HOCO$^-$. After passing into a differentially pumped chamber, the anions were accelerated to 10 keV and mass selected by time of flight before being intercepted by a linearly polarized laser. The second harmonic (386 nm, $E_{ph}=3.21$ eV) of a pulsed Ti:sapphire laser
The full 4\pi sr solid angle of photoelectrons was collected by a space focusing electron optics assembly. The time- and position-sensitive photoelectron detector allows the measurement of three-dimensional (3D) photoelectron velocities and is positioned parallel to the plane of the ion and laser beams. The photoelectron kinetic energy (eKE) resolution can be improved by discarding events with significant photoelectron velocity components perpendicular to the plane of the electron detector. The resulting photoelectron intensity distribution in these equatorially sliced photoelectron spectra is corrected based on the cylindrical symmetry about the electric vector of the laser when the laser polarization is along the ion beam and parallel to the face of the electron detector.\(^{68}\) The photoelectron kinetic energy (eKE) resolution is \(\Delta E/E \sim 13\%\) determined by the photodetachment of OH\(^-\) at 386 nm (eKE=1.38 eV).

Undetached anions were deflected out of the fast beam, while the neutral products impinged on a time- and position-sensitive detector which consists of a stack of microchannel plates and a fast-delay-line anode.\(^{69}\) Stable neutral products (HOCO radicals) arrive at the detector at a time and position determined by the velocity vector distribution that characterizes the parent HOCO\(^-\) ion packet prior to photodetachment. In the case of DPD, the time of arrival of two coincident photofragments has to differ by more than an \(\sim 17\) ns dead time of the detector. The mass ratio of the coincident photofragments (H+CO\(_2\) or OH+CO) and the center of mass (c.m.) kinetic energy release were determined by the conservation of linear momentum using the time- and position-of-arrival information.\(^{70,71}\) One has to be cautious about the large false coincidence rate in the DPD process of HOCO\(^-\) as the majority neutral products are stable HOCO free radicals and the kinetic energy release among dissociation fragments is small. An additional gating on the photofragment mass spectra was applied in data analysis procedure, reducing the false coincidence contribution to the data significantly. As a result of the large difference in masses for the H+CO\(_2\) product channel, a large fraction of the H atom products miss the detector even at a beam energy of 10 keV, so the detector acceptance function (DAF), as well as the low detection efficiency for H atoms with microchannel-plate detectors,\(^{72}\) plays an important role in the detection of this product channel. A Monte Carlo simulation has been used to calculate the DAF of the present spectrometer under these experimental conditions and correct the intensity distributions in the two dissociation product channels.\(^{73}\) The DPD of O\(_4^-\) at 532 nm was used to calibrate the neutral particle detector, yielding a resolution of \(\Delta E_T/E_T \sim 9\%\).

III. RESULTS

In accord with the previous DPD study using 4.80 eV photons, three neutral product channels were observed after the photodetachment of HOCO\(^-\) or DOCO\(^-\) at 3.21 eV. In this section, the experimental results for H/D+CO\(_2\)+e\(^-\), OH/O\(_D\)+CO+e\(^-\), and HOCO/DOCO+e\(^-\) channels will be presented separately, including the PPC spectra for both DPD channels and photoelectron spectra for the stable HOCO/DOCO channel.

### A. H/D+CO\(_2\)+e\(^-\) channel

The PPC spectra \(P(eKE,E_T)\) for the H+CO\(_2\)+e\(^-\) and D+CO\(_2\)+e\(^-\) channels resulting from the DPD of HOCO\(^-\) and DOCO\(^-\), respectively, are shown in Fig. 2. The PPC spectrum is a two-dimensional histogram where the intensity

![Fig. 2. Photoelectron-photofragment kinetic energy correlation spectra](image-url)
of each point represents the probability for the observation of an event with a specific partitioning of kinetic energy between the photoelectron (eKE) and the recoil of the neutral photofragments (ET) in the c.m. frame. The photoelectron spectrum P(eKE) displayed on the left side and the photofragment translational energy spectrum P(ET) on the bottom of the coincidence spectrum are generated by integrating over the complementary variable in the two-dimensional spectrum. As mentioned in the experimental section, only a small fraction of H products can be detected, making it necessary to DAF correct the raw coincidence spectra N(eKE,ET) to generate the final P(eKE,ET) in Fig. 2. The coincidence spectra presented here are truncated at ET =0.025 eV. This is necessary because the DAF around ET =0 rapidly approaches zero due to the dead time of the neutral particle detector and false coincidences from stable isotopes.

The two closely spaced diagonal lines I in Fig. 2 are theoretical predictions for KE\text{max}, the maximum kinetic energy release for all products (eKE+ET) in the DPD process HOCO+ +hv→H+CO2+e− at E_\text{h}=3.21 eV. The two predicted KE\text{max} values, 1.72 eV for cis-HOCO− and 1.77 eV for trans-HOCO−, are determined in the manner described by Clements et al.\textsuperscript{60} In the present experiments, there is no clear way to determine the relative population of these predicted isomers in the parent ion beam. Since no theoretical calculations on DOCO− are available, the KE\text{max} values calculated for DPD of HOCO− are also used in Fig. 2(b), showing the energetic limits qualitatively. More events extend beyond KE\text{max} in D+CO2+e− than in H+CO2+e−, because the deuterated experiment was carried out at a higher signal counting rate to minimize the consumption of the isotopic gas mixture, leading to a larger contribution of false coincidences.

Isotope effects in the DPD channel of HOCO− +hv→H+CO2+e− can be examined by comparing Figs. 2(a) and 2(b). The photoelectron kinetic energy spectrum correlated with the H+CO2 neutral product channel has a relatively broad distribution and a peak at ~1.1 eV, while the P(eKE) distribution in the D+CO2+e− channel is obviously narrower, with a peak at ~1.0 eV. In the P(ET) spectrum for H+CO2 neutral fragments, in addition to the two features at 0.43 and 0.52 eV, some evidence for a progression in the product CO2 bending mode (~0.08 eV) (Ref. 74) is observed. This progression is similar to the previous observation in a study of the DPD of HOCO−, the formate anion isomer of HOCO.\textsuperscript{75} It should be noted, however, that the formate anion has an EA ~3.49 eV (Ref. 76) and as a result has a very different photoelectron spectrum that cannot contribute to the present observations given a photon energy of 3.21 eV. Figure 2(b) shows that a similar P(ET) spectrum was observed for the D+CO2 neutral products from DPD of DOCO−, with the two major peaks shifted to 0.49 and 0.56 eV, respectively.

The horizontal line set II at eKE=0.67 eV (trans-HOCO−) and 0.62 eV (cis-HOCO−) in Fig. 2 shows the disassociation barrier c-HOCO TS2 into H+CO2 products as predicted by ab initio calculations of TS2 (Ref. 10) and the ground state anions.\textsuperscript{60} It is evident that nearly all of the eKE distribution is at higher energies than this limit, implying that dissociation into H+CO2 occurs below the calculated TS2 barrier using the assumption that the parent HOCO− anions have no internal excitation prior to photodetachment. This and other aspects of these spectra will be addressed further in Sec. IV.

B. OH/OD+CO+e− channel

DPD of HOCO− into OH+CO+e− was also observed. Figure 3 shows the PPC spectra P(eKE,ET) for DPD of (a) HOCO− +hv→OH+CO+e− and (b) DOCO− +hv→OD+CO+e−. The calculated energetic limitations KE\text{max} (0.72 eV for trans-HOCO− and 0.67 eV for cis-HOCO−)\textsuperscript{60} are marked by diagonal lines I. As Fig. 3 shows, most of the OH+CO+e− events have a total kinetic energy (KE\text{total} =eKE+ET) larger than the theoretical value of KE\text{max}. The line set II in Fig. 3 shows the experimental KE\text{max} values, ~1.25 eV for OH+CO+e− and ~1.30 eV for OD+CO+e−, respectively, which are determined from the contour at 15% of peak and represent the estimated level of false coincidences. Such significant disagreement between the absolute theoretical energy limits and the experimental results was not observed in the H+CO2+e− DPD channel, although this discrepancy is similar to the observation that the H+CO2+e− channel appears to occur below the c-HOCO TS2 barrier on the PES. To compare the current work with the previous DPD study of HOCO− at E_\text{h}=4.80 eV, the maximum available energies (1.78 eV for cis- and 1.91 eV for trans-HOCO−) predicted for photodetachment from the ground state of HOCO− to the bottom of the neutral HOCO well (CCF calculation) (Ref. 60) are also shown in Fig. 3 by lines III.

The isotope effects on the OH+CO+e− channel are not as obvious as those observed in H+CO2+e−. A Gaussian fit to the overall profile in the P(eKE) spectra correlated with the OH+CO and OD+CO neutral products yields peaks of 0.73 and 0.76 eV, respectively. However, the most intense part of the PPC spectrum for OD+CO+e− [Fig. 3(b)] definitely is displaced farther from line set I toward higher eKE compared with the PPC spectrum for OH+CO+e− [Fig. 3(a)]. In the P(eKE) spectra for OH+CO+e−, three barely resolved peaks are seen to be spaced by 0.08–0.09 eV from each other, in agreement with the predicted C–O stretching frequency in HOCO− (663 cm⁻¹ for trans- and 741 cm⁻¹ for cis-HOCO−) (Ref. 60) where O′ represents the O atom connecting the C and H atoms. Evidence for at least two of these three peaks is also observed with a shift to higher eKE in the P(KE) distribution for OD+CO+e−. The shapes of P(ET) for the OH+CO and OD+CO channels are very similar, with peaks at 0.12 and 0.15 eV, respectively.
C. Stable HOCO$^-$

As discussed in the Introduction, the photodetachment of HOCO$^-$ not only leads to the two DPD channels OH$^+$CO$^-$ and H$^+$CO$_2^-$ but predominantly yields the stable HOCO free radical. Figure 4 shows the overall photoelectron spectrum for the photodetachment of HOCO$^-$. The spectrum contains contributions from both stable and dissociative photodetachment, including dissociative events where only one of the atomic or molecular products is detected. The $P(eKE)$ peaks for HOCO$^-$ and DOCO$^-$, respectively, are at significantly higher eKes compared to either of the DPD channels H/D+CO$_2^-$ and OH/OD+CO$^-$.

As discussed by Clements et al., this is consistent with the production of stable HOCO/DOCO radicals. An analysis of the $P(eKE)$ distributions coincident with only stable HOCO radicals was carried out by including only photoelectrons detected in coincidence with a single neutral particle. In addition, for any neutral particle taken into account as a stable HOCO radical, the reconstructed 3D position of arrival at the detector was required to fall within a small spherical region centered on the parent ion beam. This effectively reduces false coincidence contributions to the stable HOCO spectrum from DPD events where only one particle, which in general recoils out of this spherical region, is detected. False coincidence contributions for the H/D+CO$_2$ channel will remain the largest, however, given the low detection efficiency for the H/D atoms and the fact that the recoil of CO$_2$ out of the ion beam is small. The resulting $P(eKE)$ spectra shown in Fig. 4(b) are shifted to higher eKE, with the peaks at 1.29 eV for stable HOCO$^-$ and 1.32 eV for stable DOCO$^-$. The eKE spectra from H/D+CO$_2^-$ and OH/OD+CO$^-$ are also summarized in Figs. 4(c) and 4(d), showing that distinct yet overlapping eKE spectra are observed for the three competing neutral product channels.

IV. DISCUSSION

The DPD of HOCO$^-$ and its deuterated form allows a direct examination of theoretical predictions of the energetics and dynamics of the HOCO free radical and the potential energy surface governing the OH+CO$^-$→H+CO$_2$ reaction. In this section, first the theoretical studies of this system will...
be used to examine the mechanisms responsible for the observations presented here. Special attention will be paid to the potential role of vibrationally excited anions in both of the DPD channels and the tunneling mechanism in the H/D/CO₂ channel. The isotope effects observed in the P(eKE, Eₚ) coincidence spectra for HOCCO⁻/DOCOCO⁻ will be discussed as well. Finally, the branching ratios for the three neutral product channels after the photodetachment of HOCCO⁻/DOCOCO⁻ will be compared with the theoretical predictions from the most recent six-dimensional quantum wave packet dynamics calculations.64

Only the ground electronic state of the HOCO radical can be accessed by the photodetachment of the HOCCO⁻ anion at Eₜₓₐₜ = 3.21 eV.60 Although all of the energy minima and saddle points shown in Fig. 1 are energetically allowed, the region of the PES where nascent HOCO radicals can be produced is restricted by the Franck-Condon overlap determined by the structure of the parent anion. The HOCO radicals with the highest energy on the PES can be expected to lead to OH + CO + e⁻ products, in competition with the more thermodynamically favorable dissociation channel leading to H + CO₂ + e⁻. Those nascent HOCO intermediates possessing the lowest energy (highest eKE) are trapped inside the deep potential well and form stable free radicals.

As mentioned in Sec. II, with the assumption that all the anions before photodetachment are in the vibrational ground state, nearly all of the H+CO₂ + e⁻ products will be formed below the cis-HOCO TS2 barrier but have enough energy to surmount the H-CO₂ barrier connecting the C₂H₂-CO₂ local minimum to H+CO₂ products. As noted before, the P(Eₚ) distributions for H+CO₂ are found to be similar to those obtained from the DPD study of HOCCO⁻,75 making it necessary to examine the possibility that HOCO intermediates dissociate into H + CO₂ over the H-CO₂ barrier, instead of passing through the most favorable reaction path involving cis-HOCO TS2 expected for a parent HOCCO⁻ anion.

DPD of the HOCCO⁻ anion can be ruled out because the 3.21 eV photon energy used in these experiments is less than the 3.49 eV required to photodetach HOCCO⁻.76 Forming the C₂H·CO₂ conformer via trans-HOCO (the expected route) is not likely either, as this isomerization involves a high calculated barrier TS4, inconsistent with the observed photoelectron spectra which show that all the HOCCO intermediates are produced with internal energies below TS4. Therefore the involvement of the H-CO₂ barrier in H+CO₂ dissociation can be ruled out assuming the parent anions are vibrationally “cold.”

If the anions were vibrationally excited, it would require 1.2 eV vibrational excitation in trans-HOCO⁻ to overcome the TS4 barrier and yield the P(eKE) spectrum seen in this experiment or 1.5 eV excitation in HOCCO⁻ to produce a P(eKE) peak at 1.1 eV. The first case is impossible since trans-HOCO⁻ would dissociate into OH⁻ + CO or H + CO₂ with such high excitation (see Fig. 1).60 For the second case regarding HOCCO⁻, even if the anions can be thermally excited by 1.5 eV, the low-lying excited electronic states of HOCO radical would be involved on the neutral PES generated by the photodetachment, and as a result a significantly different P(eKE) spectrum from Fig. 4(c) would be expected.75,76 Thus, the H-CO₂ barrier is not likely to play a role in the production of H+CO₂ in this experiment.

A second explanation is that H+CO₂ products are formed by tunneling through the cis-HOCO TS2 barrier. Several previous studies have suggested that the production of H+CO₂ by tunneling may play an important role in the OH+CO reaction.6,12,16,37 However, the tunneling effect cannot explain why the other DPD channel OH+CO + e⁻ is observed beyond the maximum energetic limits dictated by the available thermochemical data and theoretical predictions. Assuming that the theoretical calculations are correct, this disagreement can only be explained by the existence of either vibrationally excited HOCO⁻ or other, unknown, anion isomers or excited electronic states with energies higher than the theoretically predicted cis- and trans-HOCO⁻ isomers. Examination of the experimental KE max in the OH+CO + e⁻ channel [line II in Fig. 3(a)] shows that if this unknown anion isomer exists, its stability relative to OH+CO + e⁻ will be roughly ~2.0 eV, only ~0.2 eV below the OH⁻ + CO reactants. Therefore the potential involvement of weakly bonded (OH⁻)CO species in the HOCO⁻ beam must also be considered. However, as noted in the earlier study by Clements et al., the photoelectron angular distribution (PAD) for HOCO⁻ peaks parallel to the laser electric vector. This is inconsistent with a weakly perturbed OH⁻ species as the PAD of OH⁻ is perpendicular to the laser polarization.77

There is no theoretical evidence for the other anion isomer conformers such as HOOC⁻ or OHCOCO⁻ to date, although they cannot be completely ruled out.

Clements et al. proposed that either false coincidences with stable HOCO radicals or vibrationally excited HOCO⁻ must be responsible for the significant discrepancy between the experimental and theoretical KE max in the OH+CO + e⁻ channel. The longer wavelength used for photodetachment in the present work allows a more accurate measurement of the photoelectron spectra and more effective discrimination against false coincidences with additional mass gating. The most likely mechanism for the observed spectra, therefore, is the presence of vibrationally excited HOCCO⁻ in the ion beam. The evidence of hot bands in parent ions has been observed in a previous experiment studying the photodetachment of CH₃CO₂ at 355 nm. An unresolved long tail in the near-threshold region of the eKE spectrum78 was later proved to be the mixing of vibrational progressions of OCO bending in CH₃CO₂ radical and hot bands of CH₃CO₂⁻ by a photodetachment study of low-temperature CH₃CO₂⁻.79 The influence of hot bands may be more severe in the present study. As noted in the experimental section, when generating HOCCO⁻, a relatively long nozzle-skimmer distance was used, with electron impact localized near the skimmer aperture. Thus, collisional cooling of nascent HOCCO⁻ may not be effective in the limited expansion remaining. In another experiment studying the near-threshold photodetachment of HOCCO⁻ using 1.60 eV photons, evidence was seen in the photoelectron spectra for hot bands of ~0.3 eV relative to the theoretical predictions of the EA for HOCCO⁻.80 This further supports the production of a vibrationally excited, and very possibly non-thermal, distribution of HOCCO⁻ and DOCOCO⁻ anions in the source. This could explain the observation of the OH+CO...
structures annotated by “A” and “B” in the H+CO2 channel above the theoretically predicted energetic limits for KEmax by DPD of these vibrationally “hot” HOCO−. The experimental KEmax in OH+CO+e− is approximately 0.5 eV higher than the theoretical value, indicating the excitation of some of the parent anions by several quanta of C−O’ stretching, which may preferentially lead to the C−O’ bond breaking upon photodetachment and enhance the production of OH+CO. The tentative observation of a progression in the C−O’ stretch of HOCO− in the (eKE) spectra for the OH+CO+e− channel mentioned in Sec. III further supports this mechanism.

The existence of vibrationally excited parent anions in the production of OH+CO+e− is also crucial in explaining the isotope effect observed in Fig. 3(b). In DOCO−, the density of vibrational states is larger than in HOCO−, so more vibrational excitation might be expected. Therefore, the shift in the (eKE) of Fig. 3(b) to higher eKE is likely to arise from the increased population of vibrationally excited states in DOCO− and small isotopic shifts in the EA. The significant decrease of the O’−H stretching frequency in the neutral radical upon deuteration will also contribute to the observed isotope shift in (eKE) of Fig. 3(b), since the isotope shift of the vibrational frequencies in the anion is expected to be smaller due to the more anharmonic anionic PES. A detailed examination of this explanation requires extensive ab initio calculations for vibrational frequencies and ZPEs on a global PES of HOCO− and DOCO−, beyond the scope of the present study. On the other hand, little isotope effect was observed in the (P(Ef)) distributions for the recoil of OD +CO neutral products, consistent with a predicted simultaneous reduction of ZPEs and O−D stretching frequencies for the OH+CO+ channel.

It should be noted that although the experimental KEmax (line II) in Fig. 3(a) is ~0.5 eV higher than the predicted value, the discrepancy between the theoretical KEmax and the most intense feature in the (P(eKE),Ef) spectra of Fig. 3(a) is less than 0.3 eV. Assuming that a subset of the HOCO− anions are vibrationally excited by ~0.3 eV, the horizontal line set II representing the c-HOCO TS2 in Fig. 2(a) will be raised by the same amount, separating the two resolved structures annotated by “A” and “B” in the H+CO2 +e−(eKE,Ef) spectrum of Fig. 2(a). This raises the possibility that vibrationally excited HOCO− anions also play a role in the apparent production of H+CO2+e− below the c-HOCO TS2 barrier. The H+CO2+e− products may be formed by two different mechanisms simultaneously: (1) DPD of vibrationally excited HOCO− produces nascent HOCO radicals above the dissociation barrier, followed by rapid unimolecular dissociation into H+CO2 [feature A in Fig. 2(a)]; and (2) nascent HOCO radicals formed by the photodetachment of HOCO− with less vibrational excitation that tunnel through the c-HOCO TS2 barrier to form H +CO2 [feature B in Fig. 2(a)]. Assuming this mechanism, the spectrum in Fig. 2(b) indicates that in the case of DOCO−, the vibrationally excited anions play a more important role in D+CO2 formation (feature A dominates) while the probability of tunneling is reduced greatly in the case of the D atom (feature B essentially disappears). An immediate result of this explanation for the isotope effect is that most D+CO2 fragments are formed by passing over the c-HOCO TS2 barrier, yielding a narrower eKE spectrum and a shift in the (P(Ef)) distribution to higher Ef compared with the H+CO2 +e− channel that includes a significant tunneling contribution.

An alternative mechanism is that the H+CO2+e− channel is solely produced by passing over the c-HOCO TS2 barrier during DPD of vibrationally excited HOCO− and there is no tunneling effect. This is less likely as it conflicts with the evidence for the tunneling mechanism from the measurement of the product branching ratios which will be discussed in detail below. In addition, this mechanism could not explain why feature A at eKE= ~0.9 eV and feature B at eKE= ~1.1 eV in the H+CO2+e− channel merge into one narrower peak at eKE= ~1.0 eV in the D+CO2+e− channel. Another possibility, mentioned earlier, that C25H·CO2 is involved in the formation of either feature A or B can also be neglected even in the presence of anions with vibrational excitation up to ~0.3 eV, as this is not sufficient to overcome the TS4 barrier leading to the formation of C25H·CO2. Therefore the only reasonable explanation is that upon deuteration substitution, feature B disappears as the tunneling mechanism is closed, while feature A formed by the photodetachment of vibrationally excited anions shifts to higher eKE as observed in the other two channels forming OD +CO+e− and DOCO+e−.

The branching ratios for the three competing neutral product channels, stable HOCO, H+CO2, and OH+CO, can help understand the reaction mechanisms discussed above. The most reliable approach to obtaining the branching ratios is to reproduce the overall P(eKE) spectra in Fig. 4(a) by fitting the three channel-resolved eKE distributions determined in the PPC experiment, as shown in Fig. 5. The branching ratios estimated by the eKE fitting in HOCO− and
TABLE II. Branching ratios in DPD of HOCO−.

<table>
<thead>
<tr>
<th></th>
<th>Stable HOCO</th>
<th>H+CO2</th>
<th>OH+CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>258 nm</td>
<td>0.81</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>386 nm</td>
<td>0.67</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>386 nm (DOCO−)</td>
<td>0.70</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>Theory (trans)</td>
<td>0.86</td>
<td>0.03</td>
<td>0.11</td>
</tr>
<tr>
<td>Theory (cis)</td>
<td>0.89</td>
<td>0.02</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*Reference 60.

b The uncertainties of branching ratio are estimated to be ~10% of the listed value for the H/D+CO2 and OH/OD+CO channels.

c Six-dimensional wave packet calculations, Ref. 64.

DOCO− measurements are listed in Table II, along with the results from a previous DPD study of HOCO− at 258 nm and the recent calculations.

In general, both experiment and theory show that the majority of the neutral products in the DPD process of HOCO−/DOCO− are stable HOCO or DOCO radicals, qualitatively consistent with the deep potential energy well of HOCO. Comparison of the H+CO2+e− and D+CO2+e− channels at E_{ph}=3.21 eV shows a significant isotope effect as the branching ratio of this channel decreases by half in the deuterated measurement, consistent with a role for tunneling in this DPD channel as discussed above. An interesting observation is that the reduction of D+CO2 fragments is accompanied by an increase in the production of both stable DOCO and OD+CO. This can be explained by the predicted isotope effect on the HOCO PES. As calculated by Yu et al., the ZPE of the OD+CO dissociation limit decreases by 0.06 eV compared with OH+CO, while the tunneling barrier c−HOCO TS2 is only reduced by 0.02 eV upon deuterium substitution (see Table I).10 As a result, on the DOCO PES, the OD+CO ground state is 0.09 eV lower than the TS2 barrier. Thus the excess nascent DOCO radicals arising from the elimination of tunneling would not only be trapped in the DOCO well but also dissociate into ground state OD+CO, causing a simultaneous increase in the branching ratios of both OD+CO and stable DOCO.

Recently, Zhang et al. calculated branching ratios resulting from the DPD of HOCO− using six-dimensional quantum wave packet dynamics on the LTSH surface. The results are summarized in Table II for comparison with the experimental results. The theoretical work of Zhang et al. predicted that only 2%–3% of neutral products are H+CO2, which differs significantly from the experimental values, 16% for H+CO2 in DPD of HOCO− and 9% for D+CO2 in DPD of DOCO−. The theoretical branching ratio for OH+CO is also smaller than the experimental result. Consequently, the theoretical results predict that the stable HOCO product is more dominant. There are a number of potential explanations for these disagreements between theory and experiment. Based on the discussion above, the possible role played by vibrationally hot anions in the production of OH+CO and H+CO2 products is neglected in these calculations. It was also found that the calculations effectively predict no tunneling leading to H+CO2 products. This may be a consequence of the LTSH PES used in the wave packet calculation not being sufficiently accurate in the critical region around the TS2 barrier separating cis-HOCO from H+CO2 products.11 In fact, as discussed by Zhang et al., although the energy of the c-HOCO TS2 on the LTSH surface is similar to that obtained from other high-level ab initio calculations,10 the LTSH surface predicts a thicker barrier, reducing the tunneling probability.10,11 It should be noted as well that the LTSH surface was not optimized near the stationary points in the HOCO well and in fact had to be significantly rescaled to obtain a realistic Franck-Condon region.60,64 Zhang et al. also carried out Rice-Ramsperger-Kassel-Marcus calculations on the branching ratios, yielding a ratio of 1:1.2 for OH+CO:OD+CO. This is close to the ratio of 1:1:1 we found in the present E_{ph}=3.21 eV DPD experiments on HOCO−, but very different from the 2:1 ratio obtained in CCF’s measurement using 4.80 eV photons.60

The discrepancies between the two measurements at different photon energies is likely to be a result of the improved eKE resolution using a lower photon energy and the reduction of false coincidences by additional mass gating on the photofragment channels. It is clear that in spite of the impressive full-dimensional calculations of Zhang et al., a complete understanding of the DPD dynamics observed in these experiments will require more theoretical work. Accurate simulation of a DPD experiment requires fully characterized anion and neutral surfaces. In the case of the present experiments, the potential existence of vibrationally excited anions makes the characterization of the anion surface even more important. A faithful representation of the present experimental results, including vibrationally excited HOCO−, would require a reliable anion PES for trans- and cis-HOCO− in a range up to the OH+CO dissociation limit.

The wave packet calculations of Zhang et al. also predicted energy distributions for the DPD of HOCO−. In their results, the P(eKE) spectra for H+CO2+e− channel shift ~0.5 eV to higher eKE from the experimental data. This is not surprising as vibrationally excited HOCO− anions were not taken into account and negligible tunneling was found in their work. Owing to the approach used by Zhang et al., no prediction of the P(E_T) for the H+CO2 product channel was obtained. On the other hand, the theoretical P(E_T) distributions for OH+CO products are consistent with the experiment, implying that the DPD of the ground state and vibrationally excited HOCO− produces nascent neutral HOCO radicals with very similar dissociation dynamics, possibly a result of significant vibrational adiabaticity on the neutral dissociation surface. Due to the limited Franck-Condon region predicted by the LTSH PES for neutral HOCO and the harmonic anion surface in the calculation of Zhang et al., the DPD events they predicted mostly occur from the long tail extending towards the high energy side of the spectral density (Fig. 3 in Ref. 64). Therefore, a significant effect on the two DPD channels is expected if a more realistic Franck-Condon region, including vibrationally excited anions on an anharmonic surface, becomes available.

V. CONCLUSIONS

Photoelectron-photofragment coincidence spectroscopy was employed to study the DPD dynamics of HOCO− and
DOCO$^-$ at $E_{hv}=3.21$ eV, providing a useful method to probe the dynamics of the OH+CO→HOCO$^-$→H+CO$^+$ reaction on the ground state potential energy surface. The dominant neutral product formed by photodetachment was found to be stable HOCO/DOCO free radicals trapped in a deep potential well, accompanied by two dissociation channels leading to H/D+CO$_2$ and OH/OD+CO$_2$ products. It is suggested that both OH+CO and OD+CO products are formed by the DDP of vibrationally excited HOCO$^-$/DOCO$^-$. H+CO$_2$ products are produced by either the tunneling mechanism at total energies below the predicted dissociation barrier c-HOCO TS2 or unimolecular dissociation of nascent HOCO radicals above the c-HOCO TS2, formed by DDP of vibrationally excited HOCO$^-$. As a result, two resolved structures are observed in the PPC spectrum for H+CO$_2$ +e$^-$. Tunneling is reduced significantly in the DOCO$^-+hv$→D+CO$_2$+e$^-$ DDP process and the vibrationally excited DOCO$^-$ anions become the major source of D+CO$_2$ products. The results presented in this study provide evidence in favor of the tunneling mechanism suggested by some of the previous kinetics studies on the OH+CO→H+CO$_2$ reaction at low temperature. The proposed DDP mechanism is also supported by the product branching ratios. The recent quantum wave packet dynamics predictions of Zhang et al. illustrate that full-dimensionality calculations on this four-atom system are now possible and can capture essential elements of the experimental results. More extensive calculations to construct a complete anharmonic potential energy surface of HOCO$^-$ up to the OH$^+$+CO dissociation limit, as well as the stationary points for DOCO$^-$, are needed. In addition, the LTHS surface used in the simulations has known problems with the stationary points at the bottom of the HOCO well, so an improved neutral surface is also required. From an experimental perspective, a primary goal should be the elimination of any hot band contributions in the parent anions. A temperature-controlled ion trap for anion accumulation and cooling may be the best approach to solving this problem, as illustrated in a number of studies by Wang et al. Near-threshold photodetachment studies of HOCO$^-$ and DOCO$^-$ at a photon energy of 1.6 eV, characterizing the bottom of the HOCO well, will also be reported in the near future.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy (DOE) under the Grant No. DE-FG03-98ER14879. One of the authors (R.E.C.) acknowledges many useful discussions with Evelyn Goldfield and Stephen Gray.

45 D. M. Medvedev, S. K. Gray, E. M. Goldfield, M. J. Lakin, D. Troya, and...