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Valence Photoionization and Autoionization of the Formyl Radical

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ABSTRACT: We have used 308 nm photolysis of acetaldehyde to measure a photoionization spectrum of the formyl (HCO) radical between 8 and 11.5 eV using an 11 meV FWHM photoionization energy resolution. We have confirmed that the formyl radical is the carrier of the spectrum by generating an identical spectrum of the HCO product in the Cl + H₂CO reaction. The spectrum of HCO and its deuterated isotopologue (DCO) have several resolved auto-ionizing resonances above the Franck–Condon envelope, which we assign to autoionization after initial excitation into neutral 3s\sigma and 3p Rydberg states converging to the first triplet excited state of HCO⁺($\tilde{a}^{3}A'$). The quantum defects for these states are $\delta_{3s\sigma} = 1.06 \pm 0.02$ and $\delta_{3p} = 0.821 \pm 0.019$. We report absolute photoionization cross-section measurements of $\sigma_{HCO}^{PI}(9.907 \text{ eV}) = 4.5 \pm 0.9 \text{ Mb}$,



 $\sigma_{\rm HCO}^{\rm PI}(10.007 \text{ eV}) = 4.8 \pm 1.0 \text{ Mb}, \sigma_{\rm HCO}^{\rm PI}(10.107 \text{ eV}) = 6.0 \pm 1.2 \text{ Mb}, \sigma_{\rm HCO}^{\rm PI}(10.107 \text{ eV}) = 5.7 \pm 1.2 \text{ Mb},$ and $\sigma_{\rm HCO}^{\rm PI}(10.304 \text{ eV}) = 10.6 \pm 2.2 \text{ Mb}$ relative to the photoionization cross section of the methyl radical. The absolute cross-section measurements are a factor of ~1.5 larger than those determined in past studies, although the presence of strong autoionizing features supports a dependence on photoionization cross sections. We propose that the semiempirical model of Xu and Pratt for estimation of free radical photoionization cross sections is more accurate when applied with a reference species containing the same atoms as the free radical rather than isoelectronic species with different atoms.

1. INTRODUCTION

Photoionization mass spectrometry (PIMS) has emerged as a powerful tool for probing the kinetics and speciation in chemical reactions relevant to a wide range of fields, including combustion,¹ planetary atmospheres,^{2,3} and catalysis.^{4,5} The use of "soft ionization" sources (i.e., via vacuum-ultraviolet wavelengths, $\sim 6-15 \text{ eV}$) in PIMS experiments induces valence shell ionization and leaves the resulting cation with little internal energy for fragmentation. Thus, the atomic composition of detected cations often directly reflects the neutral species from which it was formed, greatly simplifying the assignment of species in mass spectra. Chemical species may also be identified by their unique photoionization (PI) spectrum (i.e., the photoionization cross section as a function of photon energy), enabling quantitative analysis of branching ratios for different isomers in complex reactions. For example, methylhydroxycarbene (CH_3 -C-OH), vinyl alcohol (H_2C =CHOH), and acetaldehyde (CH₃CHO) all give rise to a $C_2H_4O^+$ cation upon ionization, but they can be distinguished and quantified based on their PI spectra as shown in Cool et al.⁶ and Samanta et al.⁷

Free radicals are ubiquitous in gas-phase chemical reactions, and their observation and quantification can provide important validation and constraints on proposed reaction mechanisms. Although identification of a chemical species can be performed using PI spectra measured with relative intensity, quantification of species concentration requires the spectrum to be placed on an absolute basis via careful measurements of the PI cross section. Several methods for obtaining absolute cross-section measurements for stable gas-phase species exist, although below ~12.5 eV it is most common to measure an unknown PI cross section relative to a reference molecule with a well-known cross section.^{6,8} In this type of measurement the concentration ratio of the target to reference species must be known-a requirement that makes measurements of absolute PI cross sections for reactive free radical species particularly challenging. Several methods to overcome this problem have been developed and usually rely on photodissociation or pyrolysis of a stable compound to produce a well-characterized stoichiometric yield of the radical of interest and a radical with a previously determined PI cross section.⁹ Variations of this technique, comparing the cross section of a free-radical to the PI cross

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section of its stable, photolytic precursor, have also been used,¹⁰ as have approaches utilizing total carbon balance.¹¹ These studies are often complex, and thus accurate measurements require careful evaluation.

In this study we use two independent methods, photodissociation of acetaldehyde and the Cl + formaldehyde (H_2CO) reaction, to produce the ubiquitous formyl radical (HCO) and measure its PI spectrum and absolute PI cross section. Photodissociation of acetaldehyde has been used previously by Shubert and Pratt¹² to determine the absolute PI cross section of HCO, $\sigma_{\text{HCO}}^{\text{PI}}(E)$, at E = 10.257, 10.304, and 10.379 eV by comparison with the absolute PI cross section of the methyl (CH_3) radical that is produced stoichiometrically (1:1) with HCO during photodissociation. We also report a PI spectrum of DCO (produced by 308 nm photolysis of d_4 acetaldehyde) and assign resonances in the HCO and DCO spectra to autoionization via 3s and 3p Rydberg states that converge to the lowest triplet state of the cation. Finally, we apply the semiempirical method of Xu and Pratt¹³ to estimate the PI cross section of HCO and propose that H₂CO is a more appropriate analogue to HCO than is the isoelectronic molecule NO for such cross-section estimations.

2. METHODS

2.1. Multiplexed Photoionization Mass Spectrometry (MPIMS). The multiplexed photoionization mass spectrometer employed in the present work has been previously described in detail.^{9,14,15} In brief, the instrument consists of a quartz slowflow reactor coupled to a 50 kHz orthogonal time-of-flight mass spectrometer. Neutrals extracted in a molecular beam from the reactor are photoionized by quasi-continuous (500 MHz) monochromatized tunable undulator vacuum-ultraviolet (VUV) radiation from the Chemical Dynamics Beamline^{16,17} of the Advanced Light Source at Lawrence Berkeley National Laboratory. A photolytically initiated chemical reaction can be probed at a single photoionization energy (E) to obtain a data set, I(m/z, t), that is measured signal as a function of mass-tocharge (m/z) and time (t, relative to the instant of photolysis). This type of measurement can be used to determine PI cross sections for HCO, produced from the photodissociation of acetaldehyde (CH₃CHO), relative to its cofragment CH₃ at several values of E where no autoionizing resonances are observed and also at values in the vicinity of resonances for comparison with previous measurements. Because HCO and CH₃ can be ionized and detected in the same experiment, no measurement of the VUV photon flux is required, eliminating this source of systematic error. A probe of the reaction in which E is also varied yields a three-dimensional data set, I(m/z, t, E), from which we obtain photoionization spectra (photoion signal vs E) for various photodissociation and reaction products over a given interval of t. In this case, the recorded signal is normalized to the VUV photon flux, which is proportional to the measured photocurrent generated by a calibrated SXUV-100 photodiode at each value of E.

The VUV photon energy (*E*) was calibrated using the autoionizing $8s \leftarrow 5p$ transition in xenon at 12.5752 eV, as described elsewhere.⁹ The energy resolution of the ionizing VUV radiation can be increased at the expense of photon flux by narrowing the exit slit of the 3 m monochromator placed between the undulator and the experiment, and we provide specific values of this resolution in section 3. These experiments could be performed without synchrotron radiation by using tunable monochromatized VUV radiation from a discharge

lamp. However, the brightness of the source would be much lower than from a third-generation synchrotron, and hence acquisition times would be significantly longer. Emerging technologies such as cascaded harmonic generation¹⁸ may bring bright, high-repetition rate VUV sources into small laboratories in the near future.

In this work we produced HCO radicals via two independent methods: the 308 nm photodissociation of acetaldehyde, $CH_3CHO \rightarrow CH_3 + HCO_1$ and the chemical reaction Cl + $H_2CO \rightarrow HCl + HCO$. In the former, HCO was generated in a 1:1 stoichiometric ratio with CH₃ using 308 nm photolysis (4 or 10 Hz, ~50 mJ cm⁻² pulse⁻¹) of acetaldehyde ($[CH_3CHO]_0 \approx$ $(1-2) \times 10^{14} \text{ cm}^{-3}$) or d_4 -acetaldehyde (for production of DCO + CD_3) in excess He at a total pressure of 4 Torr and a temperature of 298 K. Under collisionless conditions acetaldehyde is assumed to yield predominantly CH₃ + HCO (quantum yield: 0.91 ± 0.10).¹⁹ The net quantum yield for all dissociative processes is significantly reduced with increasing pressure due to collisional deactivation of photoexcited acetaldehyde and is \sim 30% near atmospheric pressures at 308 nm.²⁰⁻²² The Stern-Volmer plots presented in Moortgat et al.²² predict that collisional deactivation is insignificant at 4 Torr. Under the assumption that collisional deactivation is negligible and by using an evaluated absorption cross section of $3.33 \times$ 10^{-20} cm² for acetaldehyde at 308 nm,²³ we estimate the initial radical concentrations of $[HCO]_0 = [CH_3]_0 \approx (2-5) \times 10^{11}$ cm⁻³ at our laser fluence. However, the present absolute crosssection measurements do not require accurate knowledge of radical concentrations as long as $[HCO]_0 = [CH_3]_0$. As discussed in more detail later, we note that HCO formed from 308 nm photolysis of acetaldehyde does not have enough internal energy to undergo secondary dissociation to form H + CO.²

All acetaldehyde + 308 nm experiments (PI spectrum and absolute cross-section measurements) were performed with \sim 11 meV FWHM resolution for *E*. Experiments used to determine the relative PI spectrum of HCO and DCO were conducted at 10 Hz photolysis rate and used data occurring between 0 and 40 ms after photolysis. Experiments used to determine absolute photoionization cross-section values for HCO were conducted at 4 Hz photolysis rate, allowing longer time windows for observing radical kinetics.

To produce HCO via the Cl + H₂CO reaction, a 300 K and 4 Torr mixture of H_2CO and oxalyl chloride ($C_2O_2Cl_2$, OxCl) in excess He was photolyzed at 351 nm. Formaldehyde was introduced into the reactor by flowing He over a sample of paraformaldehyde at ~100 Torr. The presence of formaldehyde in the paraformaldehyde vapor was confirmed by the PI spectrum of m/z = 30 (see the Supporting Information), and we estimate the concentration of formaldehyde in the reactor to be $\sim 2 \times 10^{12}$ cm⁻³ under our conditions using the known PI cross section for formaldehyde.²⁵ Using a 351 nm laser fluence of ~40 mJ cm⁻² pulse⁻¹, a 351 nm absorption cross section of 3.55×10^{-20} cm² for OxCl,²⁶ a quantum yield of 2 for Cl atom production,²⁶ and [OxCl]₀ = 2×10^{14} cm⁻³, we estimate [Cl]₀ \approx 1×10^{12} cm⁻³. Although these conditions are adequate for measuring the PI spectrum of HCO, they are far from pseudofirst-order (which would require $[Cl]_0 \ll [H_2CO]_0$), thus complicating kinetics modeling to determine initial radical concentrations and, ultimately, the absolute PI cross section of HCO. Because the sole purpose of these experiments was to confirm that HCO is indeed the species being probed in this PI spectrum, these experiments were performed with reduced

data occurring between 0 and 40 ms after photolysis. 2.2. Computational Details. Quantum chemistry calculations were performed to characterize molecular orbitals for several species and to calculate Franck-Condon factors for the HCO^+ ($\tilde{a}^{-3}A'$) \leftarrow HCO ($\tilde{X}^{-2}A'$) transition. Geometry optimization and frequency analysis were performed for HCO (\tilde{X}^2A') , HCO⁺ (\tilde{a}^3A'), H₂CO (\tilde{X}^1A_1), and NO ($\tilde{X}^2\Pi$) at the CCSD(T)/cc-pVTZ level. Molecular orbitals for HCO (\tilde{X}^2A') were generated from UHF and ROHF/6-311G calculations at the CCSD(T) optimized geometries. The orbitals were nearly indistinguishable in these two cases, with the UHF $\langle S^2 \rangle = 0.77$. Franck-Condon simulations of vibronic transitions were performed at 0 K and under the harmonic-oscillator approximation using the CCSD(T) geometries and frequencies. All calculations were performed by using the Gaussian09 software package.²⁷ Our computational results on HCO⁺ ($\tilde{a}^{3}A'$) are consistent with the more extensive CCSD(T)/aug-cc-pV5Zresults of Fortenberry et al.²⁸

3. RESULTS AND ANALYSIS

3.1. Relative Photoionization Spectrum of HCO and DCO. Photoionization spectra between 8 and 11.5 eV of the HCO radical (m/z = 29) produced by photolysis of acetaldehyde at 308 nm and the Cl + H_2CO reaction are shown in Figures 1a and 1b, respectively. Although the resolution of the VUV light used in these experiments differs (11 meV vs 26 meV), the spectra are nearly identical. The fact that the same spectrum was generated from two different methods corroborates our assignment that the photoionization spectra in Figures 1a and 1b both belong solely to the HCO radical. The time dependence of the m/z = 29 signal did not vary with E in the range explored in the present experiments, providing further support that the observed signal belongs solely to the formyl radical. We will use the higher resolution and higher signal-to-noise HCO spectrum from the acetaldehyde + 308 nm experiments in the remainder of the discussion of HCO photoionization.

The spectra exhibit a slow rise from the adiabatic ionization energy (AIE) of HCO at 8.15022 \pm 0.00006 eV²⁹ and from the AIE of DCO at $8.1353 \pm 0.0004 \text{ eV}$.³¹ The slow rise of the PI spectrum from threshold results from poor Franck-Condon overlap between the bent \tilde{X}^2A' ground state of HCO (herein termed $\tilde{X})$ and the linear X $^{1}\Sigma^{\widetilde{+}}$ ground state of the cation (herein referred to as X⁺). We estimate the end of the Franck-Condon envelope for the first photoelectron band is near 10.1 eV based on the He(I α) photoelectron spectrum of HCO reported by Dyke et al.³⁰ If direct ionization were the only ionization mechanism for HCO, we would expect the PI cross section to plateau at 10.1 eV and remain constant until the first excited electronic state of the cation became energetically available. Note that the onset of the first electronically excited state of HCO⁺ (\tilde{a} ³A') is reported to be 13.95 ± 0.05 eV above the ground state of neutral HCO.²⁸ Above 10.1 eV significant structure is observed in the HCO and DCO photoionization spectra, which we assign in section 4.1 to several autoionizing resonances. The spectra end at 11.5 eV because the CH₃CHO⁺ cation fragments into $CH_3 + HCO^+$ at energies above 11.78 eV. Formation of this fragment ion at m/z = 29 would overwhelm the signal from ionized HCO neutral that also appears at m/z =29.





Figure 1. (a) Photoionization spectrum of HCO (m/z = 29) produced by 308 nm photolysis of acetaldehyde. The AIE for HCO at 8.15022 eV^{29} is indicated by the black arrow. The red arrow indicates the end of the Franck–Condon envelope for $X^+ \leftarrow \tilde{X}$ suggested by the highest energy feature (~10.1 eV) in the HCO He(I) photoelectron spectrum reported by Dyke et al.³⁰ (b) PI spectrum of HCO (m/z = 29) produced by the Cl + H₂CO reaction. (c) PI spectrum of DCO (m/z =30) produced by 308 nm photolysis of d_4 -acetaldehyde.

The photoionization spectrum for DCO (m/z = 30) produced by 308 nm photolysis of d_4 -acetaldehyde is presented in Figure 1c. The DCO photoionization spectrum exhibits a strong similarity to the HCO spectrum in Figures 1a and 1b, although upon close inspection it is clear that many of the autoionizing resonances apparent in the HCO spectrum are not resolved in the DCO spectrum, and there are also resonance features apparent in the DCO spectrum that are not resolved in the HCO spectrum. This isotope effect will be discussed in more detail in section 4.1.

3.2. Absolute Photoionization Cross-Section Measurements. As described elsewhere,^{6,9} absolute PI cross-section measurements can be made by comparing the observed signal for an unknown species to that of a reference species if the concentration ratio of the two species is known. Photodissociation of acetaldehyde at 308 nm presents a case where HCO and CH₃ are produced in a 1:1 ratio, and the multiplexed nature of the present MPIMS experiments allows direct comparison of their signals at a single photoionization energy. Because HCO and CH₃ signals are measured simultaneously, the photon flux causing their ionization is identical, and hence the photon flux need not be measured. However, the concentrations of these radicals decay with time via a variety of bimolecular reactions and other loss processes in our reactor. Fortunately, the details of their chemical consumption are

unimportant so long as that consumption is smoothly varying with time, allowing an extrapolation of signals to time zero. Here "time zero" means after photodissociation is complete but before chemical reactions have modified the photoproduct concentrations. A process that depletes CH₃ or HCO during our instrument response time of \sim 400 μ s would cause an error in the absolute PI cross section determination, but such fast depletion via bimolecular reactions is very unlikely given the highly dilute conditions we utilize. Unimolecular decomposition of nascent HCO to H + CO could deplete the HCO concentration rapidly even under very dilute conditions, but as shown in section 4.2, this process is endothermic with 308 nm excitation and does not occur even with 266 nm excitation.³² For these reasons, the kinetics and mechanisms of CH₃ and HCO consumption do not affect the determination of the HCO absolute PI cross section as long as a proper extrapolation of their signals to time zero is performed.

Similar to our treatment in the absolute PI cross-section measurements of the propargyl and vinyl radicals,^{9,10} we fit the measured time-dependent signals (Figure 2) to a combined first-



Figure 2. Black traces show the time dependence of the (a) HCO (m/z = 29) and (b) CH₃ (m/z = 15) signal in acetaldehyde + 308 nm experiments using a photoionization energy of 10.107 eV. The experimental data were fit to a combined first- and second-order kinetics model to determine the signal at the instant of photolysis. The resulting fit is shown in red.

and second-order kinetics model to extrapolate the signals for HCO and CH₃ at time zero (see the Supporting Information and ref 9). We collect these ratios of HCO:CH₃ signal at a few discrete VUV photon energies with extended signal averaging to improve the signal-to-noise ratio and use the resulting absolute cross-section values for HCO to place our PI spectra on an absolute basis. For consistency, we used a photoionization energy resolution of ~11 meV FWHM for both the single-energy absolute cross-section measurements and our PI spectra.

An example of the measured time-dependent HCO and CH_3 signals at 10.107 eV and fits of these data to the aforementioned kinetics model are presented in Figure 2. The consistency of fits to time-dependent signal for CH_3 was significantly improved by constraining the first-order loss rate constant to nearly zero

(0.001 s⁻¹). The pseudo-first-order loss of CH₃ from its reaction with the acetaldehyde precursor is expected to be negligible (<0.001 s⁻¹) given the bimolecular rate constant for this reaction of ~10⁻¹⁷ cm³ s⁻¹ molecule⁻¹ at 300 K.³³ Heterogeneous loss of CH₃ on the walls of our quartz reactor tube is also first-order but is generally quite slow (<5 s⁻¹). This constraint had little effect on signal values extrapolated to t = 0 but served to provide more consistent values of the second-order loss term in the fitting procedure. A typical extrapolated HCO signal intensity was ~2– 3 times larger than that of the methyl radical. A complete report of the fit results is presented in Table S1 of the Supporting Information, but we emphasize they are used only to extract the signals at zero time rather than to extract rate coefficients of bimolecular reactions.

We utilize the approach of Savee et al. to determine absolute photoionization cross sections using MPIMS.⁹ Because the detection efficiency of species *i* depends on molecular mass m_i , we correct the signal for the measured mass discrimination factor⁹ in this work of $\alpha_i = m_i^{0.82\pm0.02}$. Comparing extrapolated HCO and CH₃ signals and interpolating values for the absolute photoionization cross section of CH₃ as reported in ref 34, we obtain five absolute cross-section measurements between 9.907 and 10.304 eV that are shown in Figure 3. In the region near the end of the Franck-Condon envelope (~10.1 eV), which appears free of resonances in our spectra, we determine values of $\sigma_{\text{HCO}}^{\overline{\text{PI}}}(9.907 \text{ eV}) = 4.5 \pm 0.9 \text{ Mb}, \sigma_{\text{HCO}}^{\overline{\text{PI}}}(10.007 \text{ eV}) = 4.8 \pm 1.0$ Mb, and $\sigma_{\text{HCO}}^{\text{PI}}(10.107 \text{ eV}) = 6.0 \pm 1.2 \text{ Mb}$ using a photoionization energy resolution of 11 meV FWHM. An additional measurement was performed at 10.107 eV by using half of the initial acetaldehyde concentration that was used in other experiments and yielded a value of $\sigma_{\text{HCO}}^{\text{PI}}(10.107 \text{ eV}) = 5.7$ \pm 1.2 Mb, in good agreement with the measurement at higher precursor concentration. We also performed a measurement of the cross section at 10.304 eV (yielding $\sigma_{\text{HCO}}^{\text{PI}}(10.304 \text{ eV}) = 10.6$ \pm 2.2 Mb) to compare with past determinations of σ_{HCO}^{PI} as discussed in more detail below. All five absolute measurements are used to place the relative photoionization spectrum of HCO on an absolute scale via a weighted linear least-squares fit (black circles in Figure 3 and Table S2, weights of 2σ). Reported uncertainties are 2σ values and arise largely from uncertainty in the absolute PI cross section of the methyl radical.

3.3. Vibrational Structure in the Photoionization Spectra. Figure 1 shows two distinct peak progressions in the PI spectra for HCO and DCO. The first, from 10.2 to 11.0 eV, is more defined for HCO, whereas the second, from 11.0 to 11.5 eV, is more defined for DCO, with peak widths of ~35 meV. These features likely arise from autoionizing resonances because they appear above the end of the $X^+ \leftarrow \tilde{X}$ Franck–Condon envelope (~ 10.1 eV) but before the onset of the first electronically excited state of HCO⁺ (\tilde{a} ³A'), 13.95 ± 0.05 eV above the ground state of neutral HCO.^{28,29} A narrower range of these spectra is plotted in Figure 4, along with an additional spectrum from 10.1 to 11 eV acquired at similar spectral resolution but with finer point spacing (~10 meV FWHM resolution, 5 meV steps, thin black trace in Figure 4). Within our signal-to-noise, we observe no additional structure or significant narrowing of features in the finer scan, but the peak positions may be more precisely extracted. Table 1 displays the peak positions in the two progressions along with assignments discussed in section 4.1.

8.5

9.0

Photoionization Cross-Section (Mb)

pubs.acs.org/JPCA Article 25 HCO (m/z = 29)Acetaldevde + 308 nm (present work) 20 Acetaldehyde + 308 nm (present work, scaled) Shubert and Pratt FitzPatrick et al. 15 FitzPatrick et al. (x2) 10 5

Figure 3. Absolute photoionization cross-section measurements of HCO from the present work (red squares) with error bars representing 2σ uncertainty in the measurement. A relative PI spectrum of the HCO radical scaled to the absolute cross-section measurements is shown as black circles. A PI energy resolution of 11 meV FWHM was used in both sets of measurements. Absolute PI cross-section measurements of HCO reported by Shubert and Pratt¹² at significantly higher energy resolution are presented as green triangles. The absolute cross section for HCO reported by FitzPatrick et al.³⁵ is shown as blue diamonds, and a scaled version of their spectrum is shown as a dashed blue line to illustrate its similar shape to the spectrum measured in the present work.

Photoionization Energy (eV)

10.0

9.5



Figure 4. Expanded view of the 10.1-11.5 eV region of the HCO and DCO PI spectra where resolved autoionizing resonances appear. The combs that are overlaid on the spectra over the $3s\sigma \leftarrow \tilde{X}$ and $3p \leftarrow \tilde{X}$ features are spaced by the calculated harmonic C-O stretch frequency for the ã⁺state of HCO⁺ or DCO⁺ as reported by Fortenberry et al.,² i.e., $v_3^{\text{H}} = 1539 \text{ cm}^{-1} (0.191 \text{ eV}) \text{ and } v_3^{\text{D}} = 1523 \text{ cm}^{-1} (0.189 \text{ eV}).$

4. DISCUSSION

The present work marks the first experimental observation of resonance structures in the photoionization spectrum of HCO and DCO, and we begin with a discussion of their origins. We then compare our measurements of $\sigma_{\rm HCO}^{\rm PI}$ with the smaller values reported by Shubert and Pratt¹² and FitzPatrick et al.³⁵ Finally, we compare our directly measured cross sections of HCO with a semiempirical model of Xu and Pratt for estimating photoionization cross sections of free radicals using more easily obtained cross sections of stable species.¹³

11.0

11.5

10.5

4.1. Autoionizing Resonances. Despite their potential importance in the dissociative recombination of HCO⁺ with free electrons, very few studies have examined excited states of neutral HCO that lie above the AIE (i.e., "superexcited" states). $^{29,36-39}$ In the absence of a detailed understanding of electronic states of neutral HCO that exist between the AIE of HCO at 8.15 and 11.6 eV (the highest energy probed in the present experiments), the most plausible superexcited states of HCO for initial consideration are those in the Rydberg series leading to the second ionization limit $(\tilde{a}^+ {}^{3}A')$. As discussed below, the autoionizing features we observe are consistent with two series converging to this limit. Fortenberry et al.²⁸ have recently performed high-level ab

initio calculations on the \tilde{a}^+ state of HCO⁺, which is formed by removal of a 6a' π -bonding electron from HCO (leaving the 7a' antibonding electron in the highest occupied molecular orbital), leading to a bent nuclear configuration. Their calculations place the \tilde{a}^+ state 5.80 \pm 0.05 eV above the HCO⁺(X ${}^{1}\Sigma^+$) state (including zero point correction), which places the \tilde{a}^+ state 13.95 \pm 0.05 eV above HCO(\tilde{X}). Removal of the 6a' π -bonding electron causes significant C–O bond elongation from 1.18 Å in \tilde{X} to 1.27 Å in \tilde{a}^+ , whereas there are only modest changes to the equilibrium C–H bond length (1.13 to 1.12 Å) and bond angle \angle H–C–O (125° to 118°) in the transition from \tilde{X} to $\tilde{a}^{+.28}$ These geometry changes support some degree of C–O (ν_3) stretch excitation for $\tilde{a}^+ \leftarrow \tilde{X}$ transitions. Because a diffuse Rydberg electron should not substantially affect bonding, Rydberg states converging to \tilde{a}^+ should have nearly identical geometries, vibrational frequencies, and vibrational progressions as HCO \tilde{a}^+ . Fortenberry et al. calculated a frequency of $\nu_3 = 1539$ cm⁻¹ (0.191 eV) for the C–O stretching mode of $HCO(\tilde{a}^+)$ and $\nu_3 = 1523 \text{ cm}^{-1}$ (0.189 eV) for DCO(\tilde{a}^+),²⁸ in reasonable agreement with the spacing of features in the PI spectrum measured here (see Table 1 and Figure 4). We calculated Franck–Condon factors for the $\tilde{a}^+ \leftarrow \tilde{X}$ transition in HCO and

Fable 1. Peak Center Energies o	of HCO and	l DCO Extracted	l from tl	he Data in	Figure 4 ^{<i>a</i>}
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	peak center (eV) uncertainties 2σ			vibrational assignment	
isotopologue	25 meV steps	5 meV steps	Rydberg series	quantum number	peak spacing (cm ⁻¹)
НСО	10.325	10.325 ± 0.011	$3s\sigma$	$\nu_{3}{}' = 0$	
	10.500	10.503 ± 0.007		$\nu_{3}{'} = 1$	1436 ± 100
	10.688	10.668 ± 0.006		$\nu_{3}{'} = 2$	1331 ± 75
	10.865	10.852 ± 0.008		$\nu_{3}{'} = 3$	1484 ± 80
DCO	11.084 ± 0.015		3p	$\nu_{3}{}' = 0$	
	11.276 ± 0.014			$\nu_{3}{'} = 1$	1549 ± 160
	11.461 ± 0.013			$\nu_{3}{'} = 2$	1492 ± 150
^a Vibrational progress	sions in the C–O stretch	(ν_3') are built on the c	origins of both the $3s\sigma$	and the 3p Rydberg state	28.

DCO under the harmonic approximation at the CCSD(T)/ccpVTZ level (see Figure S3). As expected, the strongest progression is in the C–O stretch (ν_3), which peaks at $\nu = 1$ and extends to $\nu = 5$.

We assign the peaks in Table 1 to two different Rydberg series for two reasons. First, the gap between the fourth and fifth resolved peaks is $\sim 1880 \text{ cm}^{-1}$, significantly larger than the gaps between any other adjacent pair of peaks, providing evidence that these two peaks do not belong to the same progression. Although the higher energy vibrational progression is taken from the DCO spectrum, whereas the lower energy progression is from HCO, the 1880 cm^{-1} gap between the two progressions is large compared to the 1% isotopic frequency shift in ν_3 between HCO and DCO. Second, it would be hard to explain the significant rise in ion signal near 11.0 eV (peaks 5–7 in Table 1) if these peaks were simply an extension of the progression of the first four peaks. Instead, the observed intensity increase is consistent with the origin of a second Rydberg state with a larger absorption cross section and/or a larger probability for autoionization (perhaps resulting from a lower probability for predissociation) compared to the first state. We therefore assign the origin transitions of the first and second Rydberg states as 10.325 ± 0.011 and 11.084 ± 0.015 eV, respectively.

Given these origin assignments, the Rydberg formula (eq 1) may be used to evaluate the quantum defect, δ , associated with these autoionizing states by using the origin transition energies (E_{Ryd}) , the ionization energy of the cation to which they converge $(E_{\text{ion}} = 13.95 \pm 0.05 \text{ eV} \text{ for } \tilde{a}^+)$,^{28,29} and an effective principal quantum number (n).

$$E_{\rm Ryd} = E_{\rm ion} - \frac{R}{(n-\delta)^2} \tag{1}$$

 $R = 109737 \text{ cm}^{-1} (13.6057 \text{ eV})$ is the Rydberg constant. Because the valence molecular orbitals of HCO arise from combinations of n = 2 atomic orbitals, it is logical to choose n = 3 as the first guess for the principal quantum number of these Rydberg states. This approach leads to quantum defects of $\delta = 1.06 \pm 0.02$ for the transition at E_{Ryd} = 10.325 eV and δ = 0.821 ± 0.019 for the transition at E_{Rvd} = 11.084 eV. The quantum defect of δ = 1.06 for the first state is in reasonable agreement with the quantum defect of the $3s\sigma$ Rydberg series in the isoelectronic NO radical $(\delta = 1.104)^{41}$ and in formaldehyde $(\delta = 1.107)^{42}$. The value of δ = 0.821 for the second series lies in between the quantum defects for the $3p\sigma$ and $3p\pi$ of formaldehyde $[\delta(3p\sigma) = 0.768, \delta(3p\pi) =$ 0.835] and agrees reasonably well with the measured quantum defects in the 3p states of NO [$\delta(3p\sigma) = 0.735$, $\delta(3p\pi) =$ 0.782)]. We observe only one set of peaks consistent with a 3p Rydberg series and cannot differentiate between the $3p\sigma$ and $3p\pi$ possibilities, although these might be separable and

assignable with higher spectral resolution than is possible in our experiments. They may both contribute to our observed signal. Further evidence that H₂CO is a better analogue to HCO than the isoelectronic molecule NO is given in section 4.3. Note that if we assign the two origin transitions to n = 4, eq 1 returns quantum defects of $\delta = 2.06$ and $\delta = 1.821$. These quantum defects disagree drastically with the known Rydberg spectroscopy of H₂CO and NO, and we therefore discard this assignment.

On the basis of this agreement with quantum defects for similar species, we assign the observed features to autoionization of vibrationally excited $3s\sigma$ and 3p Rydberg states of HCO that converge to \tilde{a}^+ . Figure 5 shows an energy level diagram summarizing our results with predicted positions for the remaining members of the $ns\sigma$ and np series using $\delta_{s\sigma} = 1.06$ and $\delta_p = 0.821$. All $n \ge 4$ Rydberg states should appear above 12.4 eV and are therefore not observed in our spectra.

The 6a' HOMO-1 orbital of HCO that is involved in these electronic transitions cannot be approximated by a simple



Figure 5. Energy level diagram of the HCO system. The *nso* (blue) and *np* (red) Rydberg series converge to the HCO⁺(\tilde{a} ³A') excited state. Observed vibrational levels in the ν_3 mode (C–O stretch) are labeled with vibrational quanta for the 3s σ (blue) and 3p (red) Rydberg states.

atomic orbital (Figure 6), and hence the atomic Rydberg selection rule of $\Delta l = \pm 1$ is not expected to hold, enabling the

HOMO - 1







Figure 6. Three orthogonal views of the HOMO-1 (6a') for the \tilde{X} state of HCO calculated at the UHF/6-311G level by using CCSD(T)/cc-PVTZ geometries. Excitation from this orbital gives rise to the \tilde{a}^+ state of the cation and associated Rydberg states observed in this work.

observation of both s and p Rydberg series. The contribution of autoionizing resonances to the total photoionization cross section are related to the absorption cross sections for the $3s\sigma \leftarrow \tilde{X}$ and $3p \leftarrow \tilde{X}$ transitions and also the rate at which autoionization of these superexcited states competes with other decay processes. These dependencies can be used to qualitatively support the shape of the HCO spectrum above the Franck–Condon envelope (~10.1 eV, above which direct ionization should provide no additional intensity) in light of our spectroscopic assignments.

First, the large increase in the intensity of the $3p \leftarrow \tilde{X}$ spectral feature (starting at 11.05 eV) when compared to the increase observed at the onset of the $3s\sigma \leftarrow \tilde{X}$ feature (~10.1 eV) is likely due to overlap between the $3p\sigma \leftarrow \tilde{X}$ and $3p\pi \leftarrow \tilde{X}$ transitions. Assuming quantum defects for the $3p\sigma$ and $3p\pi$ states of NO⁴¹

and formaldehyde⁴² suggests spacing of only 0.12–0.17 eV between the $3p\sigma$ and $3p\pi$ states of HCO. Thus, the increased intensity above 11.05 eV and the barely resolved vibrational structures for HCO may simply represent the overlap of the $3p\sigma$ and $3p\pi$ states. An increased autoionization rate or a decreased rate of competing decay processes (e.g., dissociation and fluorescence) for the 3p states relative to the $3s\sigma$ states may also contribute to the observed intensity differences in the photoionization cross section associated with these features.

At present, we cannot explain the observation that the vibrational peaks in the $3s\sigma$ state are barely resolved for DCO, whereas the vibrational peaks in the 3p state are barely resolved for HCO. Because autoionization from the bent Rydberg states to the continuum of the linear HCO⁺ $X(^{1}\Sigma^{+})$ state involves bending excitation, it is likely that the bending mode couples the Rydberg states to the continuum. Deuteration significantly decreases the frequency of this mode ($v_2^{\rm H} = 939 \text{ cm}^{-1} \text{ vs } v_2^{\rm D} = 733$ cm^{-1}),²⁸ which likely affects the relative rates of autoionization between HCO and DCO. The ~35 meV peak widths for the better resolved peaks we observe correspond to an uncertainty broadened lifetime of \sim 19 fs, which is less than one bending period. If the broadening of spectral features were based solely on the rate of autoionization, we would expect the features to be more pronounced in DCO. However, this is not the case for the $3s\sigma \leftarrow X$ region of the DCO spectrum, and it may suggest more complex mechanisms are at play. Future studies exploring the photoionization, photoabsorption, and photodissociation dynamics in this energetic region would aid in the interpretation of observations made here.

4.2. Comparison with Other Absolute Measurements. Using ion imaging and a four-wave mixing scheme for generation of VUV light, Shubert and Pratt¹² ionized the CH₃ and HCO products produced from 266 nm photodissociation of acetaldehyde to determine $\sigma_{\rm HCO}^{\rm PI}$ relative to $\sigma_{\rm CH_3}^{\rm PI}$. Their resulting values of $\sigma_{\text{HCO}}^{\text{PI}}(10.257 \text{ eV}) = 4.8 \pm \frac{2.0}{1.5} \text{ Mb}, \sigma_{\text{HCO}}^{\text{PI}}(10.304 \text{ eV}) = 5.9 \pm \frac{2.2}{1.6} \text{ Mb}, \text{ and } \sigma_{\text{HCO}}^{\text{PI}}(10.379 \text{ eV}) = 3.7 \pm \frac{1.2}{1.2} \text{ Mb}$ are presented alongside the absolute measurements from this work in Figure 3. FitzPatrick et al.³⁵ employed a crossed laser molecular beam apparatus coupled with undulator-generated tunable VUV radiation (~0.4 eV bandwidth, National Synchrotron Radiation Research Center, NSRRC) to create a 1:1 ratio of ethene (C_2H_4) and HCO from secondary dissociation of C_3H_5O fragments produced by 193 nm photolysis of epichlorohydrin (c-(CH₂OCH)CH₂Cl). Their determination of $\sigma_{\text{HCO}}^{\text{Pl}}$ was performed relative to the well-known cross section for ethene at 11.27 $eV_{,0}^{6}$ and similar to the present work, this single-energy cross-section value was used to place a relative HCO spectrum on an absolute scale. After one corrects for the differences in spectral resolution, the absolute spectrum obtained by FitzPatrick et al., presented in Figure 3, agrees well with the shape of the present spectrum but implies cross-section values that are in agreement with those reported by Shubert and Pratt and smaller than the values determined in the present work.

Interpolation of our absolute photoionization spectrum for HCO at 10.257, 10.304, and 10.379 eV (i.e., the photon energies used by Shubert and Pratt) yields respective cross-section values of 7.3, 9.0, and 9.2 Mb (with ~20% uncertainties), which suggest a cross section that is a factor of ~1.5 larger than that reported by Shubert and Pratt. Because our method and theirs both rely on $\sigma_{\rm CH_3}^{\rm PI}$, we recently obtained an absolute photoionization spectrum for the methyl radical with improved signal-tonoise,⁹ which yields $\sigma_{\rm CH_3}^{\rm PI}$ values that are systematically ~10%

lower than those used by Shubert and Pratt. However, reducing their $\sigma_{CH_3}^{PI}$ values by 10% would decrease their determinations of σ_{HCO}^{PI} by 10%, causing an even larger discrepancy with the present work.

Shubert and Pratt dissociated acetaldehvde with 266 nm radiation, depositing ~107 kcal/mol of energy into acetaldehyde. Subtracting the C–C bond dissociation energy of $82.79 \pm$ 0.07 kcal/mol²⁴ leaves \sim 24 kcal/mol of available energy to be partitioned between translational energy and internal degrees of freedom of CH₃ and HCO. It is energetically feasible for some HCO products to contain enough energy to undergo secondary dissociation to H + CO $(D_0 = 14.54 \pm 0.02 \text{ kcal/mol})$.²⁴ The resulting overestimation of the relative concentration of HCO would cause an underestimation of σ_{HCO}^{PI} . However, Shubert and Pratt observed a translational energy distribution of HCO similar in shape to that for the CH₃ coproduct; if a significant amount of HCO were decaying to H + CO, the HCO distributions would be depleted at low translational energies. Similarly, Toulson et al.³² performed time-resolved ion imaging dissociation experiments on acetaldehyde at 266 nm and found no evidence for secondary dissociation of HCO. Therefore, it is unlikely that this process could account for the factor of 1.5 by which the present absolute cross-section measurements differ from the values determined by Shubert and Pratt.

The bandwidth of the VUV light generated in the four-wave mixing scheme employed by Shubert and Pratt is likely to be much narrower (<0.1 meV FWHM) than the 11 meV FWHM VUV radiation used here. At higher resolution, the region near the origin transition at 10.325 eV might exhibit larger amplitude fluctuations due to autoionizing features sharper than we can resolve in our moderate resolution spectra (Figures 1 and 2). If Shubert and Pratt chose a photon energy in a valley between two closely spaced, sharp autoionizing peaks, where direct ionization would dominate, this choice could explain the discrepancy in absolute cross-section determinations. Our absolute photoionization spectrum near the end of the $X^+ \leftarrow \tilde{X}$ Franck-Condon envelope at 10.1 eV gives $\sigma_{\text{HCO}}^{\text{PI}}(10.1 \text{ eV}) = 5.9 \pm 1.2$ Mb, which agrees reasonably well with Shubert and Pratt's cross sections if their values are at a baseline value between resonance peaks.

In our experiments HCO undergoes a collision with the helium bath gas approximately every 25 ns. Therefore, within our instrument response time of ~400 μ s, it suffers ~16000 collisions before ionization, and thermalization to the ambient 298 K temperature is therefore highly likely. Because the lowest vibrational frequency of HCO($\tilde{X}~^2A')$ is 1081 cm $^{-1},^{43}$ a 298 K sample of HCO is almost entirely in its zero point level. In the experiments by Shubert and Pratt, HCO is produced in the collisionless confines of a molecular beam, and it could plausibly contain more vibrational energy than our thermal HCO product. These differences in initial distributions of vibrational energy could lead to different Franck-Condon intensities for the absorption process that ultimately gives rise to the autoionizing structure in the energetic region where Pratt and Shubert determined $\sigma_{\rm HCO}^{\rm PI}$, marking another potential source of the discrepancy in absolute $\sigma_{\rm HCO}^{\rm PI}$ measurements.

The absolute measurements by FitzPatrick et al.³⁵ were taken at a lower energy resolution than the present work. As shown in Figure 3, multiplying the FitzPatrick et al. spectrum by a factor of \sim 2 brings it into reasonable agreement with the absolute HCO cross-section measurements in the present work.

In the experiments performed by FitzPatrick et al., the HCO radical was generated by 193 nm photodissociation of epichlorohydrin (c-(CH₂OCH)CH₂Cl), with a presumed 1:1 stoichiometric ratio for production of C₂H₄ and HCO to measure σ_{HCO}^{PI} relative to C₂H₄. Similar to the Shubert and Pratt experiments, if a portion of the HCO in FitzPatrick et al. undergoes secondary decomposition and is not accounted for, the derived value of $\sigma_{
m HCO}^{
m Pl}$ would be lower than the true value. From an energetic standpoint 193 nm excitation of c- $(CH_2OCH)CH_2Cl$ can access the four-body $Cl + C_2H_4 + H +$ CO channel, which has an estimated asymptote that is exothermic with respect to the initial photolytic excitation by \sim 2.4 eV.⁴⁴ However, forward-convolution methods produced seemingly good fits to all measured velocity distributions, and it seems unlikely that FitzPatrick would obtain a good match for $HCO + C_2H_4$ components if over 50% of the HCO produced underwent secondary dissociation.

Although the present absolute cross section disagrees with previous measurements, the simplicity of the chemical system employed in our study combined with the inability for HCO to decay via secondary dissociation gives us confidence in our approach. In the next section we examine the absolute cross sections in relation to the semiempirical model presented by Xu and Pratt.¹³

4.3. Comparison with Semiempirical Model. In their study of the absolute photoionization cross section of the propargyl radical, Xu and Pratt¹³ presented a semiempirical method for estimating absolute cross-section values for free radicals based on properties of related stable molecules for which there is generally more available information. This method begins by identifying stable molecules with known photoionization cross sections and molecular orbitals that are comparable to the radical of interest. Then, the cross section for the known species at the energy of the last photoelectron band for the relevant molecular orbital (i.e., above the Franck-Condon envelope) is scaled by the orbital occupancies of the reference and radical species. More involved methods must be invoked if an orbital other than the HOMO of the stable molecule is used. With the caveat that this method works best when direct ionization is dominant, this method yields a photoionization cross section for the radical at an energy just above the Franck-Condon envelope.

As discussed in the previous section, we measure $\sigma_{\text{HCO}}^{\text{PI}}$ at the end of the X⁺ $\leftarrow \tilde{X}$ Franck–Condon envelope to be $\sigma_{\text{HCO}}^{\text{PI}}(10.1 \text{ eV}) = 5.9 \pm 1.2 \text{ Mb}$, with an onset for the $\tilde{a}^+ \leftarrow \tilde{X}$ ionization limit not expected to occur until 13.95 eV.²⁸ Because no plateau in cross section appears above 10.1 eV, the photoionization spectrum above 10.1 eV is influenced by indirect as well as direct ionization processes. Therefore, our measured value is best regarded as an upper limit of $\sigma_{\text{HCO}}^{\text{PI}}$ for comparison with values extracted from the semiempirical model.

The formyl radical has an electronic configuration of (core) $3a'^24a'^25a'^21a''^26a'^27a'^1$ in the bent neutral electronic ground state ($\tilde{X} {}^2A'$),⁴⁵ and the first photoionization limit ($X^+ \leftarrow \tilde{X}$) is characterized by removal of the 7a' HOMO electron that as described by Shubert and Pratt exhibits in-plane d_{yz} atomic-like orbital structure (shown in Figure 7). Shubert and Pratt noted a similarity between this molecular orbital and the more symmetric HOMO of the isoelectronic NO molecule (also shown in Figure 7), which has a photoionization cross section of 2.7 Mb above the end of the $X^+ \leftarrow X$ photoelectron band near 10.9 eV.^{46,47} In an atom, ionization of a d electron can produce only p and f outgoing partial waves. They argued that ionization





Figure 7. Three orthogonal views of the highest occupied molecular orbitals (HOMOs) for the ground electronic states of HCO, NO, and H_2 CO calculated at the UHF or HF/6-311G level using CCSD(T)/cc-PVTZ geometries.

from this molecular orbital, which is very similar in shape to an atomic d orbital, would lead primarily to p and f outgoing partial waves and that the matrix elements for $f \leftarrow d$ transitions would be small due to the much higher centrifugal barrier produced by the outgoing l = 3 f-wave compared to the lower centrifugal barrier of the l = 1 p-wave. Reduced intensity from $f \leftarrow d$ transitions would therefore lead to an unusually small ionization cross section.

We present this empirical model applied toward another analogue of HCO, the closed-shell molecule formaldehyde (H₂CO). Although formaldehyde is not isoelectronic with HCO, it is composed of the same atoms, giving it a chemical similarity. Brint et al.⁴² studied the VUV absorption spectrum of H₂CO below its first ionization limit, observing strong s, p, d, and f Rydberg series. They concluded that the HOMO of H₂CO must deviate substantially from any atomic-like orbital approximation and assigned this behavior to the high charge density associated with the H protons compounded by the short C–H bond lengths that places these protons close to the heavy atoms. By contrast, the Rydberg spectra of NO show that its HOMO can be approximated much more accurately in an atomic-like picture.⁴¹ We believe this difference is the main reason that H₂CO is a better analogue for HCO than is NO.

As shown in Figure 7, the HOMOs of HCO and H₂CO are both more extended than the HOMO of NO. The HOMO of formaldehyde exhibits a d_{yz} atomic-like shape similar to the more distorted HOMO of HCO (see Figure 7). The photoelectron band corresponding to removal of an electron from the H₂CO HOMO ends at ~11.3 eV,⁴⁸ where its photoionization cross section is $\sigma_{\rm H_2CO}^{\rm PI}(11.3 \text{ eV}) = 12.8 \text{ Mb}.^{25}$ Taking into account that a singly occupied orbital should have half the cross section of a doubly occupied orbital within this model, the H₂CO reference yields an estimate of 6.4 Mb for $\sigma_{\rm HCO}^{\rm PI}$, in good agreement with our measured value of $\sigma_{\rm HCO}^{\rm PI}(10.1 \text{ eV}) = 5.9 \pm 1.2$ Mb. We therefore propose that in applying the Xu and Pratt semi-empirical model to doublet free radicals, a closed-shell reference composed of the same atoms as the free radical will provide a better estimate than an isoelectronic reference molecule that contains a different atom (NO in this case).

5. CONCLUSIONS

The present work reveals the highest resolution photoionization spectrum of the HCO radical near its first ionization threshold to date. The spectra of HCO and its deuterated isotopologue DCO reveal several autoionizing resonances that have not been observed before, and we attribute these resonances to excitation of Rydberg states converging to the lowest triplet excited state of $HCO^+(\tilde{a}^{-3}A')$. Absolute cross-section values for HCO determined here relative to the photoionization cross section of the methyl radical are significantly larger than previously reported values.^{12,35} It is likely that the presence of autoionizing resonances makes cross-section measurements highly dependent on the resolution of the ionizing radiation. By use of the semiempirical method for estimating photoionization cross sections that was presented by Xu and Pratt, it appears that predictions of the HCO cross section above the first band in the photoelectron spectrum is more accurate using a reference species with similar atomic composition (i.e., H₂CO) rather than an isoelectronic species (i.e., NO). Future studies of absolute photoionization cross sections for free radicals that provide additional tests of this predictive tool would be of great interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c01775.

Kinetic fitting method and fit parameters for HCO and CH₃, tabulated absolute photoionization cross section for HCO, photoionization spectra for H₂CO, CH₃, and CD₃, and calculated photoelectron spectrum of the HCO⁺(\tilde{a} ³A') \leftarrow HCO(\tilde{X} ²A') transition (PDF)

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Notes

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