VUV Photoionization Cross Sections of HO₂, H₂O₂, and H₂CO

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Supporting Information

ABSTRACT: The absolute vacuum ultraviolet (VUV) photoionization spectra of the hydroperoxyl radical (HO₂), hydrogen peroxide (H₂O₂), and formaldehyde (H₂CO) have been measured from their first ionization thresholds to 12.008 eV. HO₂, H₂O₂, and H₂CO were generated from the oxidation of methanol initiated by pulsed-laser-photolysis of Cl₂ in a low-pressure slow flow reactor. Reactants, intermediates, and products were detected by time-resolved multiplexed synchrotron photoionization mass spectrometry. Absolute concentrations were obtained from the time-dependent photoion signals by modeling the kinetics of the methanol oxidation chemistry. Photoionization cross sections were determined at several photon energies relative to the cross section of methanol, which was in turn determined relative to that of propene. These measurements were used to place relative photoionization spectra of HO₂, H₂O₂, and H₂CO on an absolute scale, resulting in absolute photoionization spectra.



1. INTRODUCTION

Synchrotron photoionization mass spectrometry has seen increasing use in the study of gas phase free radical reactions.¹ Photoionization provides a nearly universal method for the detection of small molecules with high sensitivity. Bayes pioneered the use of photoionization mass spectrometric detection of gas phase free radicals in flow tubes,² and this technique has become an important tool for time-resolved kinetics studies in combustion and atmospheric chemistry as well as astrochemistry.^{3–9} Whereas earlier studies used quadrupole mass filters, which allowed the detection of ions with a single mass-to-charge ratio (m/z) at a time, the introduction of pulsed-extraction time-of-flight mass spectrometers gave a multiplex advantage, because one could measure the evolution of the full mass spectrum in real time.^{6,8} Dynamics experiments have further exploited the additional multiplexing that comes from imaging the ion kinetic energy distributions.^{10,11}

Recently, Osborn, Taatjes, and co-workers developed a multiplexed photoionization mass spectrometer (MPIMS), a significant advance in this technique, by using tunable vacuum ultraviolet (VUV) radiation from a synchrotron as the photoionization light source, coupled to either a double-focusing sector mass spectrometer or an orthogonal acceleration time-of-flight (OA-TOF) mass spectrometer.^{12,13} This approach exploits the high photon flux, wide tunability, and spectral resolution of modern synchrotron VUV light sources by enabling one to obtain complete, well-resolved photo-ionization spectra (photoion signal vs photon energy) at each mass and kinetic reaction time. Isomers of a given sum formula can be resolved by their unique photoionization spectra,¹² and

the multiplexing advantage allows measurement of isomerspecific chemical kinetics. 14,15

Accurate photoionization cross sections are necessary in MPIMS chemical kinetics studies to quantify the concentrations of reactants, intermediates, and products. The photoionization cross section of a stable molecule can be measured by ionizing a binary mixture of that molecule and a reference standard. From the ratio of the ion signals of these two species, their known concentrations, and the absolute photoionization cross section of the reference standard, the unknown molecule's cross section may be placed on an absolute basis.^{16,17} This method requires that the molar ratio of the two compounds in the binary mixture does not vary with time-a requirement not easily satisfied when one of the two species is reactive. Moreover, even measuring cross sections of stable molecules can present a challenge if they have low vapor pressures, are prone to polymerization, or cannot be supplied as pure samples.

Measurements of photoionization cross sections for polyatomic free radicals and other transient intermediates are challenging due to the difficulty in producing these species with detectable and quantifiable concentrations. As a consequence, photoionization cross sections for free radicals are commonly measured relative to a reference compound that is formed simultaneously with the target free radical in specific molar ratios. There is a growing body of studies that measure cross

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sections for free radical species important to the chemical kinetics of combustion and the atmosphere. $^{\rm 18-32}$

To provide an example of the complex techniques that have been employed to measure free radical photoionization cross sections, we consider three different approaches applied to the methyl radical. The first method for measuring the CH₃ cross section is to form radicals by photodissociation of a suitable precursor generating stoichiometric photofragments. Taatjes et al.¹⁸ followed this approach by photolyzing CH₃I and determined the CH₃ cross section relative to the known cross section of I from the yields of the momentum-matched photofragments. In the same study, Taaties et al.¹⁸ also used photolysis to generate methyl radicals with a known quantum yield from a precursor molecule (acetone or methyl vinyl ketone); however, in this time-dependent method using a flowreactor setup, the observed depletion of the precursor, whose photoionization cross section is known, was used to quantify the initial CH₃ number density. The initial radical signal, as determined from the radical decay kinetics, was used to obtain the photoionization cross section of CH₃ relative to the cross section of the precursor. Gans et al.¹⁹ used a similar approach, employing pyrolysis of CH₃I and CH₃NO₂, to measure the CH₃ cross section. The third approach to measuring the CH₃ cross section used a detailed kinetics model to predict the decay of CH₃ in the presence of NO₂.²⁰ Simulated CH₃ and NO time profiles (NO forms from reaction of CH₃ and NO₂) were used to provide a quantitative relationship between the CH₃ and NO signals, yielding a methyl radical cross section relative to the known NO cross section. Given the complexity of these efforts to measure the CH₃ photoionization cross section, there is remarkable agreement among the results. These three techniques have been used to obtain absolute photoionization cross sections for a variety of free radicals.²¹⁻³

In this work, we measured absolute photoionization spectra for three important species relevant to hydrocarbon oxidation, namely the hydroperoxyl radical (HO₂), hydrogen peroxide (H₂O₂), and formaldehyde (H₂CO). These species were formed in a flow reactor through a set of reactions initiated by Cl₂ photolysis in a methanol/O₂/Cl₂/He gas mixture. We measured absolute precursor depletions and used detailed chemical kinetics modeling to quantify the concentrations of all relevant species. We measured the photoionization cross sections relative to that of the methanol precursor, which in turn was determined relative to the known absolute cross section of a standard, propene.

2. EXPERIMENT

The MPIMS instrument has been described in detail in previous publications.^{12,13} The key features will be summarized in the following sections.

Briefly, we used MPIMS to probe the products resulting from laser flash photolysis of $Cl_2/CH_3OH/O_2/He$ mixtures in a slow flow reactor. An excimer laser propagated along the reactor axis, collinear with the gas flow, generating ~10¹³ cm⁻³ radicals at room temperature and 2.5–8 Torr total pressure. Products were sampled and detected using the MPIMS apparatus coupled to tunable VUV radiation from the Chemical Dynamics Beamline of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.

2.1. Multiplexed Photoionization Mass Spectrometer. The slow flow reactor was a 62 cm long, 1.05 cm inner diameter quartz tube with the inner wall coated with a fluoropolymer solution (either DuPont AF 400S2-100-1 (experiments 1–18, 23) or Cytonix FluoroPel PFC 1102 V-FS (experiments 19–22)) to minimize wall reactions. Helium (Matheson Tri-Gas, 99.9999%), Cl₂ (Matheson Tri-Gas, 5.2% Cl₂ in He), O₂ (Matheson Tri-Gas, 99.998%), and CH₃OH (manometrically prepared mixture of 4.667% methanol (Sigma-Aldrich, 99.93%, purified by three freeze–pump–thaw cycles) with balance of He) were introduced into the reactor using calibrated mass flow controllers (MKS Instruments), with a total flow of 200 \pm 1.2 sccm, unless otherwise noted. The total pressure was maintained at 2.50 \pm 0.01 to 8.00 \pm 0.04 Torr (measured with a capacitance manometer (MKS Baratron)) by throttling a Roots pump in the exhaust line.

Typical starting mole fractions of reagent gases were 30– 60% O₂, 0.3–0.6% Cl₂, and 0.1–0.2% CH₃OH with balance of He. Approximately 1% of the Cl₂ was photolyzed by the unfocused excimer pulse (Coherent COMPex Pro 110 XeF, 351 nm, 15 ns, 4 Hz) at typical laser fluences of 28 mJ cm⁻² pulse⁻¹, leading to initial radical concentrations on the order of $\sim 10^{13}$ cm⁻³. In separate experiments we measured the absolute photoionization spectrum of methanol relative to propene (Matheson Tri-Gas, 1.00% in Ar) (Supporting Information).

The reactive mixture was sampled through a pinhole in the side wall of the reactor tube, expanded into the source chamber and passed through a skimmer (1.5 mm diameter) to form a nearly effusive molecular beam in a first differential chamber (pressure $\sim 10^{-6}$ Torr). The beam was intersected ~ 2.4 cm from the pinhole by quasi-continuous (500 MHz repetition rate) synchrotron undulator-generated VUV radiation.^{13,33,34} Formed cations were accelerated and collimated into the acceleration region of a 50 kHz pulsed OA-TOF mass spectrometer and detected by a time-sensitive microchannel plate detector. The resolution of the OA-TOF mass spectrometer $(m/\Delta m)$ was ~1000 for these experiments. The time-of-flight spectrum was accumulated in a single-start, multiple-stop time-to-digital converter. We recorded full mass spectra every 20 μ s, from 20 ms before the photolysis laser pulse to 130 ms after the pulse, providing information about the kinetics in the flow tube at all detected m/z ratios. Typically, we averaged 2400-10 000 laser shots for twodimensional kinetics experiments (ion counts vs kinetic time and m/z). Time dependencies of individual species were obtained by integrating over the corresponding mass peaks at each time interval. We detected each species (HO_2, H_2O_2) H₂CO, CH₃OH, and Cl₂) at its parent m/z, with no dissociative ionization expected near its respective threshold energy.^{35–38} Table 1 summarizes the neutral species detected,

Table 1. Photon Energies for Each Species Detected in the Single-Energy Experiments a

species	m/z	AIE (eV)	photon energies used (eV)
H ₂ CO	30.011	10.889 ^b	10.90, 11.00, 11.20, 11.40, 11.45
CH ₃ OH	32.026	10.846 ^c	10.90, 11.00, 11.20, 11.40, 11.45
HO_2	32.998	11.352 ^d	11.40, 11.45
¹³ CH ₃ OH	33.030		10.90, 11.00, 11.20, 11.40, 11.45
H_2O_2	34.005	10.631 ^d	10.90, 11.00, 11.20, 11.40, 11.45
CH3 ¹⁸ OH	34.030		10.90, 11.00, 11.20, 11.40, 11.45
Cl_2	69.938	11.481 ^e	11.40, 11.45
35Cl37Cl	71.935		11.40, 11.45
³⁷ Cl ₂	73.932		11.40, 11.45

^{*a*}All species were detected at their parent ion m/z. ^{*b*}Niu et al.³⁶ ^{*c*}Macneil and Dixon.³⁵ ^{*d*}Litorja and Ruscic.³⁸ ^eYencha et al.³⁷

the m/z of the observed ion, and the photon energies used. Cl₂ and HO₂ were only detected at 11.40 and 11.45 eV due to their high ionization thresholds.

The VUV radiation first passed through a gas filter (30 Torr Ar) to remove higher harmonics.³³ We observed no evidence of ionization by higher harmonic photons presumably leaking through the gas filter. This observation is confirmed by the absence of He ions, dissociation products (e.g., HCO⁺ from H₂CO⁺), and ion signals below the literature IE for measured spectra. The VUV photons were then dispersed using a 3 m monochromator. Typically, monochromator slit widths of 50–100 μ m led to a photon rate of ~10¹³ photons s⁻¹ with an energy bandwidth of better than $\Delta E(\text{fwhm}) = 9$ meV. The exit slit of the monochromator was sometimes further narrowed as needed to reduce the photon flux and prevent saturation of the ion detector.

To record photoionization spectra, we scanned the energy of the ionizing photons from the synchrotron source from 10.508 to 12.008 eV in steps of 0.025 eV, generating three-dimensional data (i.e., ion signal as a function of m/z, kinetic time, and photoionization energy). Photoionization spectra were normalized to the photon flux measured at each photon energy with an SXUV100 photodiode placed after the photoionization volume. We daily calibrated the photon energy axis by measurement of the 8s \leftarrow 5p Xe atomic resonance, observing day-to-day changes less than 10 meV.

2.2. Photoionization Cross Section Determination. The absolute photoionization cross section of a target species ("i") can be obtained relative to a reference species ("ref") using gas mixtures with known concentrations of both species.³⁹ The time- and energy-dependent signal *S* of a species i is equal to the product of an energy-dependent scale factor C(E), which includes all instrument-specific, non-mass-dependent parameters including collection efficiency and photon flux, a mass-dependent discrimination factor α_i specific to the experimental apparatus, the energy-dependent photoionization cross section $\sigma_i(E)$, and the time-dependent concentration [N_i](t).

$$S_{i}(E,t) = C(E)\alpha_{i}\sigma_{i}(E)[N_{i}](t)$$
(E1)

The mass discrimination factor, $\alpha_i = m_i^{0.643 \pm 0.086}$, was determined empirically for this instrument.³⁰

The scale factor *C* is a constant for a given set of experimental conditions (number of shots, ion optics settings, VUV intensity). It can be determined experimentally by measuring the ion counts for a reference species for which $[N_{ref}](t)$ and $\sigma_{ref}(E)$ are already known. When counting two independent photoions from a single multiplexed experiment, we can determine the unknown species' cross section relative to the reference species from the value of *C* determined from the reference compound. The time-dependent concentrations of the unknown species i, $[N_i](t)$, come from the kinetics model. The absolute cross section of i, $\sigma_i(E)$, which must be consistent at all times *t*, is obtained by fitting the observed ion signal $S_i(E,t)$ to the modeled $[N_i](t)$ over a time interval for which the kinetic model is valid.

In some cases, two species were present with the same nominal m/z. At the two masses where this presented a problem (m/z = 33 and 34), the mass resolution of the OA-TOF spectrometer was sufficient to partially resolve the two peaks. Figure 1a demonstrates the fits achieved when only one species is present (H₂CO) whereas the following two panels demonstrate the extraction technique used to separate (b) HO₂



Figure 1. Sample time-of-flight spectra: (a) m/z = 30, containing a contribution from only one species, H_2CO^+ , which is fit with a Voigt distribution; (b) m/z = 33, containing contributions from HO_2^+ and $^{13}CH_3OH^+$; (c) m/z = 34, contains $H_2O_2^+$ and $CH_3^{18}OH^+$. Thus, m/z = 33 and 34 were fit with a linear combination of two Voigt distributions. Data are taken from experiment 23 (Table 3). The gray hashed areas in (b) and (c) indicate the regions that were integrated and renormalized to produce the final unencumbered data sets (Supporting Information).

from ${}^{13}CH_3OH$ and (c) H_2O_2 from $CH_3{}^{18}OH$. Details of the separation approach are given in the Supporting Information.

2.3. Instrument Response Function. As detailed elsewhere, there is a finite instrument response function (IRF) arising from sampling a Maxwell–Boltzmann distribution of velocities in the flow cell.⁴⁰ Measurement of the time dependence of photochemically generated species revealed that there was a slower-than-expected IRF and a slight gradient in the photolysis yield along the axis of the reactor. We characterized these effects by performing additional experi-

ments using NO_2 photolysis in which the NO product was formed instantaneously.

The first instrumental effect is a temporal IRF by (1) the transport of gas from the reactor to the ionization region and (2) the ion transit time from the ionization region to the extraction region.⁴⁰ These effects broaden the time dependence observed in the ion signal. The second effect is a variation in the excimer laser fluence along the axial dimension of the flow reactor. The latter effect is primarily ascribed to divergence of the laser beam. This gradient in photolysis energy results in comparatively higher radical concentrations at the top of the flow tube than at the pinhole. This spatial gradient of radical concentration, which is established immediately following the excimer laser pulse at t = 0, is observed as an increase in the t = 0 radical concentrations as the gas flows down the tube toward the sampling pinhole.

We characterized these two effects by performing a calibration experiment with NO₂ photolysis,

$$NO_2 + hv (351 \text{ nm}) \rightarrow NO + O(^{3}P)$$

followed by rapid O(³P) removal by the subsequent reaction with NO₂ ($k_{298K} = 1.04 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$):⁴¹⁻⁴³

$$NO_2 + O(^{3}P) \rightarrow NO + O_2$$

Photolysis of NO₂ occurs on the subpicosecond time scale and reaction of NO₂ with O atoms occurs on the 0.1 ms time scale at $[NO_2] = 1.9 \times 10^{15} \text{ cm}^{-3}$. Thus, NO₂ depletion and NO product formation are essentially instantaneous compared to the time binning (0.2 ms bin size) used in the present experiments. The time traces for both species should appear as step functions that promptly reach a constant value. However, the IRF will broaden the transition times of both signals, whereas the photolysis gradient will result in a slight increase in NO and decrease in NO₂ signal at longer times.

The instrument responses measured for the NO₂ photolysis system were convolved with the simulated kinetic profiles for the $Cl_2/CH_3OH/O_2$ system. Further details on these experiments are given in the Supporting Information.



Figure 2. Typical raw H_2CO^+ (black circles), HO_2^+ (red triangles), and $H_2O_2^+$ (green pluses) signals versus time, collected at a photon energy of 11.45 eV. The H_2CO signal is larger due to its higher cross section at 11.45 eV than those of HO_2 and H_2O_2 , resulting in an order of magnitude more counts, even though H_2CO and HO_2 have comparable number densities. The data are taken from experiment 6 (Table 3).

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3. RESULTS

3.1. Kinetics Methodology. Flash photolysis of $Cl_2/CH_3OH/O_2/He$ mixtures is a straightforward technique for generating HO₂ radicals, H₂O₂, and H₂CO, as it has a relatively simple chemistry.^{41,44–57} The 351 nm photolysis of Cl_2 generates Cl atoms essentially instantaneously

$$Cl_2 + hv (351 \text{ nm}) \to 2Cl \tag{1}$$

The Cl atoms exclusively abstract a methyl hydrogen from methanol to form CH_2OH :

$$CH_3OH + Cl \rightarrow CH_2OH + HCl$$
 (2)

 CH_2OH subsequently reacts with O_2 to form HO_2 and H_2CO :

$$CH_2OH + O_2 \rightarrow HO_2 + H_2CO$$
(3)

Under our conditions, HO₂ reacts primarily via self-reaction:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{4}$$

Neglecting secondary reactions for the moment (see below), reactions 1-4 quantitatively link the molar consumption of CH₃OH and Cl₂ with the molar production of HO₂, H₂O₂, and H₂CO.

Figure 2 shows typical time-dependent ion counts of HO_2^+ (triangles), $H_2O_2^+$ (pluses), and H_2CO^+ (circles). Dwell times were 0.02 ms and binned to 0.2 ms. We collected signal in the 20 ms before the excimer fired to establish a baseline for each m/z and then collected signal until 130 ms after the excimer pulse to follow the time-dependent concentration. The excimer fires at t = 0. All products were fully removed from the reaction region before beginning the next cycle.

To fit the observed kinetics, we employed a comprehensive model (using the Kintecus software package).⁵⁸ Table 2 shows the most important reactions. The majority of the rate coefficients were taken directly from the NASA Panel for Data Evaluation of Chemical Kinetics and Photochemical Data.⁴¹ Table S1 demonstrates the rest of the 40-reaction model (Supporting Information).

Table 3 lists initial reactant concentrations for all experiments. These concentrations were used to simulate the time-dependent concentrations of Cl_2 , methanol, HO_2 , H_2O_2 , and H_2CO .

To predict absolute product concentrations from our model, we needed to determine absolute initial Cl atom concentrations. Cl atoms could not be observed directly, both because they could not be ionized at the highest photon energy used and because the short expected lifetime (~ 1 ms) of the Cl atoms is on the same order as the IRF. Instead, we used two independent methods to determine the initial Cl atom concentration. First, we measured the fraction of Cl₂ photolyzed from the depletion of its ion signal, measured for ³⁵Cl₂⁺, ${}^{37}\text{Cl}^{35}\text{Cl}^+$, and/or ${}^{37}\text{Cl}_2^+$. Although the adiabatic ionization energy of Cl_2 is AIE = 11.481 eV,³⁷ enough signal could be observed to measure Cl₂ depletions at 11.40 and 11.45 eV. We therefore determined the Cl atom concentration from the photolysis fraction and the known Cl₂ concentration, as determined by the mass flows. In the second method, we modeled the observed time dependence of the methanol signal. Most of the CH₃OH depletion was due to the nearly instantaneous Cl + CH₃OH reaction after photolysis, with some additional chemistry from chain chlorination and trace OH radicals. Cl₂ depletion was determined only at photon

Table 2. Subset of the Reactions Used To Simulate the Concentration-Dependent Profiles for CH_3OH , HO_2 , H_2O_2 , and H_2CO^a

		$k_{298K} (\rm cm^3 \ s^{-1})$
(1)	$\operatorname{Cl}_2 \xrightarrow{h\nu} 2\operatorname{Cl}$	
(2)	$\rm CH_3OH + \rm Cl \rightarrow \rm CH_2OH + \rm HCl$	$5.5^{+1.1}_{-0.9} \times 10^{-11}$
(3)	$\mathrm{CH_2OH} + \mathrm{O_2} \rightarrow \mathrm{HO_2} + \mathrm{H_2CO}$	$9.1^{+2.7}_{-2.1} \times 10^{-12}$
(4)	$\mathrm{HO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	$(1.4 \pm 0.2) \times 10^{-12}$
(5)	$HO_2 + Cl \rightarrow HCl + O_2$	$3.5^{+0.7}_{-0.6} \times 10^{-11}$
(3)	\rightarrow OH + ClO	$1.0^{+0.4}_{-0.3} \times 10^{-11}$
$(6)^{b}$	$Cl + H_2CO \rightarrow HCO + HCl$	$7.2^{+1.1}_{-0.9} \times 10^{-11}$
(-)h	$HO_2 + H_2CO \xrightarrow{M} HOCH_2O_2$	$7.9^{+7.9}_{-3.9} \times 10^{-14}$
(7)	$\text{HOCH}_2\text{O}_2 \xrightarrow{\text{M}} \text{HO}_2 + \text{H}_2\text{CO}$	$1.5^{+1.5}_{-0.8} \times 10^2 (s^{-1})$
(8)	$\rm HCO + O_2 \rightarrow \rm HO_2 + \rm CO$	$5.2^{+2.1}_{-1.5} \times 10^{-12}$
(9) ^c	$\mathrm{CH_2OH} + \mathrm{Cl_2} \rightarrow \mathrm{ClCH_2OH} + \mathrm{Cl}$	$(2.9 \pm 0.3) \times 10^{-11}$
(10)	$HO_2 + ClO \rightarrow HOCl + O_2$	$6.9^{+1.4}_{-1.1} \times 10^{-12}$
(11)	$CH_3OH + OH \rightarrow CH_2OH + H_2O$	$7.7^{+0.8}_{-0.7} \times 10^{-13}$
	\rightarrow CH ₃ O + H ₂ O	$(1.4 \pm 0.1) \times 10^{-13}$

^{*a*}Rate coefficients for 11 of the key reactions are listed here; the values for the remaining 29 reactions are given in Table S1 (Supporting Information). Pressure-dependent rate coefficients are for 8 Torr. All rate coefficients are taken from the NASA Data Evaluation⁴¹ unless otherwise noted. ^{*b*}Taken from IUPAC.⁴⁴ ^{*c*}Taken from Tyndall et al.⁹⁴

energies \geq 11.40 eV, but CH₃OH was detected in all experiments.

Figure 3 shows examples of observed Cl₂ and CH₃OH depletions. The depletions were small (0.79 \pm 0.04% for 35 Cl³⁷Cl⁺ and 2.82 \pm 0.06% for CH₃OH⁺) but were statistically significant when averaged over the 200 points from -20 to +20 ms. The Cl atom concentrations derived from these two *in situ* measurements were in good agreement with each other and agreed well with depletions of 0.90% Cl₂ and 3.6% CH₃OH estimated using the measured laser fluence (28 mJ cm⁻² pulse⁻¹).

Table 3 lists the Cl atom concentration for each experiment. As discussed in the Supporting Information, the Cl atom concentration formed from photolysis had a slight negative gradient from the top to the bottom of the flow tube. The reported value is the mean $[Cl]_{t=0}$ derived from the Cl_2 or methanol depletions in the first 20 ms after photolysis. The measured depletion was consistent in all experiments and ranged from 0.72 \pm 0.04% to 0.81 \pm 0.05%. Chlorine atom concentrations ranged from $(0.3-3.4) \times 10^{13}$ cm⁻³. The uncertainty in the Cl concentration in a typical experiment was $\approx 6\%$.

 H_2CO was expected to form rapidly after the reaction of Cl with methanol and reach its maximum concentration in the first 0.2 ms. After the initial rise, H_2CO should not undergo further reaction, and its concentration should remain constant at the maximum value until it is pumped out.

We determined the final H_2CO concentration from the Cl atom concentration as derived above. From reactions 2 and 3, each Cl atom results in the formation of one H_2CO molecule.

Table 3. Photon Energies and Initial Concentrations for All Experiments^a

experiment	photon energy (eV)	10^{-14} [CH ₃ OH] (cm ⁻³)	$10^{-16}[O_2] (cm^{-3})$	10^{-14} [Cl ₂] (cm ⁻³)	10^{-13} [Cl] (cm ⁻³)
1	11.45	3.75	7.80	8.09	1.22 ± 0.07
2	10.90	3.75	7.80	8.09	1.22 ± 0.07
3	11.00	3.75	7.80	8.09	1.22 ± 0.07
4	11.20	3.75	7.80	8.09	1.22 ± 0.07
5	11.40	3.75	7.80	8.09	1.22 ± 0.07
6	11.45	3.76	15.6	8.08	1.22 ± 0.07
7^b	11.45	1.21	2.45	2.53	0.38 ± 0.02
8	11.45	3.77	7.80	8.09	1.22 ± 0.07
9	11.45	3.76	7.80	16.20	2.4 ± 0.1
10	11.45	3.77	7.80	8.09	1.17 ± 0.07
11	11.45	3.76	7.80	2.04	0.30 ± 0.02
12 ^c	11.45	1.94	3.90	3.99	0.57 ± 0.03
13 ^c	11.45	1.94	7.78	3.98	0.57 ± 0.03
14 ^c	10.90	1.94	7.78	3.98	0.57 ± 0.03
15 ^c	11.40	1.94	7.78	3.98	0.57 ± 0.03
16 ^c	11.20	1.94	7.78	3.98	0.57 ± 0.03
17 ^d	11.45	3.63	7.78	8.09	1.32 ± 0.08
18 ^d	11.45	3.63	7.78	8.09	1.32 ± 0.08
19	11.45	3.24	7.78	7.78	1.7 ± 0.1
20	10.90	3.24	7.78	7.78	1.7 ± 0.1
21	11.45	3.24	7.78	15.60	3.4 ± 0.2
22	10.90	3.24	7.78	15.60	3.4 ± 0.2
23, photon energy scan	10.508-12.008	3.52	7.78	8.09	1.32 ± 0.08

^{*a*}Twenty-two single-energy experiments were conducted to determine absolute energy-dependent photoionization cross sections at five photon energies (given in Table 4). Also listed are the experimental conditions used in photon energy scans used to obtain the full photoionization spectra (given in Table 5). All experiments were performed at 298 K. Experiments were performed at 8 Torr and 200 sccm total flow rate unless otherwise noted. The Cl atom concentrations listed here were measured as the average observed depletion in the Cl₂ and/or methanol signals from -20 to +20 ms. ^{*b*}Experiment conducted at 2.5 Torr. ^{*c*}Experiment conducted at 4 Torr. ^{*d*}Experiment conducted with 400 sccm total flow rate.



Figure 3. Representative observed precursor depletions for constraining radical concentrations: (a) Cl_{22} detected at m/z = 72 ($^{35}\text{Cl}^{37}\text{Cl}^{+}$); (b) methanol, detected at m/z = 32 (CH_3OH^+). Model depletion fit (red line) to the data (fitting window -20 to +20 ms). The kinetics model includes the IRF and the photolysis gradient. The experimental data are taken from experiment 6 at 11.45 eV (Table 3).

However, the final modeled H_2CO concentration was ~6% lower than the initial Cl atom concentration due to secondary reactions of Cl. In particular, reaction 5 consumes one Cl atom and reaction 6 consumes one Cl atom and one H_2CO molecule.

$$HO_{2} + Cl \rightarrow HCl + O_{2}$$

$$\rightarrow OH + ClO$$
(5)

$$Cl + H_2CO \rightarrow HCO + HCl$$
 (6)

OH reacts with methanol, leading to additional CH_2OH radicals; however, the OH densities produced by reaction 5 were sufficiently low that they had <0.2% effect on the title molecule yields. H₂CO could potentially form an adduct with HO₂, but this reaction was unimportant under our low-pressure conditions:

$$HO_2 + H_2CO \underset{M}{\stackrel{M}{\rightleftharpoons}} HOCH_2O_2$$
(7)

To first order, one HO₂ radical should be formed for each Cl atom; however, secondary chemistry, primarily HO₂ + Cl (reaction 5) resulted in a slightly lower maximum value. The expected maximum concentration of HO₂ was slightly higher than H₂CO because reaction 6 results in the effective loss of two H₂CO molecules, forming one HCO radical that contributes to a net gain of one HO₂ radical by reaction 8.

$$HCO + O_2 \rightarrow HO_2 + CO \tag{8}$$

In the absence of additional chemistry, H_2O_2 should form at half the rate of HO₂ decay.

3.2. Single Energy Cross Sections. We determined absolute photoionization cross sections for HO_2 , H_2O_2 , and H_2CO at a subset of photon energies using methanol as the photoionization cross section reference. Initial radical concentrations were determined from the measured depletion of radical precursors with known concentrations (i.e., Cl_2 and CH_3OH). Time-dependent concentrations of HO_2 , H_2O_2 , and H_2CO were determined from the kinetics model.

3.2.a. Observed Kinetics. We collected photoion signals of Cl_2 , CH_3OH , HO_2 , H_2O_2 , and H_2CO from -20 to +60 ms relative to the excimer laser pulse. Figure 4 shows typical time traces for H_2CO , HO_2 , and H_2O_2 for a representative experiment (experiment 6, Table 3) at 11.45 eV where all species of interest were observed (including CH_3OH and Cl_2).

Figure 4a shows a representative H_2CO^+ time-dependent signal. As expected, the signal rises promptly and then levels off. However, in the first few milliseconds after photolysis, the observed H_2CO^+ signal rises slightly slower than predicted by the kinetics model alone and also has a slow rise at long times (10–60 ms). We can largely correct for these deviations by using the IRF and photolysis gradients reported in the Supporting Information.

Figure 4b shows a representative time-dependent signal of HO_2^+ . HO_2 rises rapidly through reactions 2 and 3, similarly to H_2CO . The signal then decays, primarily due to self-reaction 4, with a half-life of ~20 ms. A small additional contribution to the HO_2 decay is discernible at long times, which we assign to wall reactions as described below.

The rise of $H_2O_2^+$ (Figure 4c) reflects the decay of HO_2 at times <20 ms but levels off at longer times, in contradiction with the kinetics model. We can explain this reduced yield by a combination of HO_2 and H_2O_2 wall losses as described in the following section.

3.2.b. Wall Loss. We observed loss of HO₂ and H₂O₂ at longer times (t > 20 ms) that could not be explained by gas phase reactions or pump out. We assigned these losses to heterogeneous loss at the walls of the flow tube.

In the low-pressure slow flow reactor all species within the flow tube collided with the walls of the reactor many times before exiting the pinhole. It is well-known that both HO₂ and H₂O₂ are lost to wall reactions in similar flow reactors.^{59–63} We coated the walls with fluoropolymer to reduce wall reactions. In the absence of coatings, we observed that a significant fraction of the products remained in the flow cell, even after complete pump out was expected (t > 100 ms). With coatings, this problem was eliminated. However, we still observed that HO₂ disappeared at a rate slightly faster than predicted by our model, whereas the H₂O₂ appearance rate and total yield were lower than predicted. These losses varied from coating to coating.

We found that the measured time-dependent signals and modeled species concentrations show significantly improved agreement by invoking typical wall loss rates for HO₂ and H₂O₂ of 5-12 and 5-15 s⁻¹, respectively. These rates were significantly slower than the chemical rates and had a small, though not insignificant, impact on the final concentrations and cross sections.

3.2.c. Photoionization Cross Sections. We conducted twenty-two experiments (Table 3) to measure absolute



Figure 4. Single energy kinetic traces for title molecules. Data are scaled to the model as part of the cross section determination process. Representative time-dependent traces of (a) H_2CO^+ , (b) HO_2^+ , and (c) $H_2O_2^+$ at 11.45 eV. These data are from experiment 6 (Table 3). Modeled kinetics (red line), convolved with the IRF and including a photolysis gradient and first-order wall losses of HO_2 and H_2O_2 (9.8 and 12.0 s⁻¹, respectively).

photoionization cross sections of HO₂, H_2O_2 , and H_2CO at five discrete photon energies: 10.90, 11.00, 11.20, 11.40, and 11.45 eV. We measured the photoionization cross section (Table 4) of a pure methanol sample relative to propene at each of these photon energies (Supporting Information).

In each single energy experiment, we obtained the absolute cross section for HO_2 , H_2O_2 , and H_2CO by solving for the optimal values of the wall loss rates to obtain the best fit to the time-dependent concentrations. The final cross sections, obtained from averaging several individual determinations, are given in Table 4.

3.3. Absolute Photoionization Spectra. We collected relative photoionization spectra for HO_2 , H_2O_2 , and H_2CO

Table 4. Photoionization Cross Sections for H_2CO , HO_{2} , and H_2O_2 , Determined from Single Energy Experiments^{*a*}

photon energy (eV)	CH ₃ OH (Mb)	HO ₂ (Mb)	H_2O_2 (Mb)	H ₂ CO (Mb)
10.90	2.3 ± 0.5		0.40 ± 0.12	7.3 ± 1.5
11.00	4.4 ± 0.9		0.93 ± 0.22	9.6 ± 1.9
11.20	7.5 ± 1.5		1.8 ± 0.4	12.4 ± 2.5
11.40	10.2 ± 2.0	1.1 ± 0.3	3.6 ± 0.9	14.1 ± 2.9
11.45	10.7 ± 2.1	1.3 ± 0.3	4.6 ± 1.2	14.0 ± 3.0

"Reported here are the average values at each energy. The uncertainty includes all systematic and random errors discussed in the text. Also reported are the CH₃OH cross sections, measured relative to propene (Supporting Information), that were used as the reference cross sections in each single energy experiment.

from 10.508 to 12.008 eV at 0.025 eV steps (100 μ m slit widths, corresponding to 9 meV fwhm), averaging 300 repetitions for each step, and data was integrated over 0-60 ms (Table 3, experiment 23). We placed the relative photoionization spectra on an absolute basis by fitting each spectrum to the absolute cross sections measured at all discrete photon energies. Table 5 reports the resulting absolute photoionization spectrum for each species; these spectra are also shown in Figures 5-7. The photoionization spectrum collected for the m/z = 32 peak contains only contributions from CH₃OH, making it an acceptable reference compound with no interfering isobaric species at all photon energies used here (Supporting Information). As seen in Figure S2 (Supporting Information), normalization to the photon flux did not fully remove interference from Ar absorption resonances (at 11.62 and 11.83 eV⁶⁴) in the VUV harmonic filter. The interferences caused by the Ar filter are especially apparent in the H₂CO spectrum and are noted on the figures with blue asterisks. Spectra for HO₂ and H₂O₂ were obtained using the isobaric signal separation method described above. We note that these spectra are free from contamination by the corresponding isobaric methanol isotopologue, which would grow in quickly at about 10.8 eV (Figure S2, Supporting Information); this validates our separation and extraction procedure.

3.4. Error Analysis. Several sources of error contribute to the overall uncertainty in the reported single energy cross section measurements. The uncertainty primarily stems from error in (1) absolute methanol cross section, (2) modeled concentrations of HO₂, H₂O₂, and H₂CO, and (3) random noise in the data.

The HO₂, H₂O₂, and H₂CO absolute cross sections were measured relative to the cross section of CH₃OH, which in turn was measured relative to propene, using the methodology reported in Welz et al.⁶⁵ (Supporting Information). We propagated the 20% systematic uncertainty in the reference cross section of methanol^{65,66} as part of the systematic error in the HO₂, H₂O₂, and H₂CO absolute cross section values.

The error in rate coefficients used in the kinetics model (Table 2, 1σ error bars) is propagated through the model to determine the time-dependent standard deviation of concentrations of CH₃OH, HO₂, H₂O₂, and H₂CO. For each experiment listed in Table 3, uncertainties were estimated by running 100 simulations with Monte Carlo sampling of the rate coefficient uncertainties. Typical concentration uncertainties introduced by the kinetic model were CH₃OH 0.1%, HO₂ 8%, H₂O₂ 12%, and H₂CO 2%, and were determined mostly by uncertainties in the HO₂ + HO₂ rate coefficient.

Table 5. Absolute Photoionizatior	Spectra	for HO ₂ ,	H ₂ O ₂ ,	and H ₂ CO ^a
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photon energy (eV)	HO_2 (Mb)	H_2O_2 (Mb)	H_2CO (Mb)	photon energy (eV)	HO_2 (Mb)	H_2O_2 (Mb)	H_2CO (Mb)	
10.508	0.014	0.013	-0.003	11.333	0.160	3.572	12.742	
10.533	0.000	-0.029	0.000	11.358	0.579	3.415	12.949	
10.558	0.000	0.026	0.001	11.383	0.836	3.707	13.101	
10.583	-0.004	-0.014	0.001	11.408	1.235	3.554	13.082	
10.608	0.014	0.065	0.003	11.433	1.258	4.545	13.241	
10.633	0.004	0.063	-0.009	11.458	1.253	4.028	13.193	
10.658	0.000	0.075	0.003	11.483	1.246	4.558	13.129	
10.683	0.013	0.087	-0.002	11.508	1.574	4.437	13.190	
10.708	0.000	0.194	0.010	11.533	2.059	4.627	13.322	
10.733	0.004	0.135	0.033	11.558	2.552	5.393	13.438	
10.758	0.002	0.163	0.039	11.583	2.582	5.385	13.574	
10.783	0.030	0.167	0.079	11.608	2.858	6.056	13.241	
10.808	-0.005	0.221	0.164	11.633	3.039	7.086	15.110	
10.833	0.006	0.382	0.403	11.658	3.234	6.790	14.705	
10.858	-0.040	0.351	1.999	11.683	3.226	6.430	13.373	
10.883	-0.047	0.514	6.242	11.708	3.584	6.936	14.585	
10.908	-0.011	0.579	9.221	11.733	3.951	7.546	15.137	
10.933	0.021	0.667	9.874	11.758	4.363	7.772	15.088	
10.958	0.100	0.672	9.853	11.783	4.843	8.055	13.966	
10.983	0.022	0.752	9.912	11.808	4.018	7.912	12.132	
11.008	0.077	1.213	10.429	11.833	4.494	7.583	12.564	
11.033	0.024	1.282	11.010	11.858	5.146	10.227	15.955	
11.058	0.042	1.760	11.040	11.883	5.795	10.667	16.730	
11.108	0.016	1.694	11.593	11.908	5.685	11.255	16.562	
11.133	0.071	1.751	11.877	11.933	6.123	10.756	16.336	
11.158	0.044	2.309	11.886	11.958	6.033	12.249	16.045	
11.183	0.077	1.937	12.081	11.983	5.923	11.906	15.842	
11.208	-0.014	2.114	12.319	12.008	5.806	12.877	15.927	
11.233	0.003	2.338	12.524	^{<i>a</i>} A relative spectrum w	as scaled to abs	solute measurem	ents as outlined	
11.258	-0.004	2.219	12.593	in the text. Overall un	certainties, enco	ompassing the s	ystematic error	
11.283	-0.119	3.446	12.594	described in the text: HO ₂ , 21%; H ₂ O ₂ , 23%; H ₂ CO, 20%. The da				
11.308	-0.084	2.598	12.845	point at 11.083 eV has been removed (Supporting Information).				

We repeated several experiments at each photon energy. The cross sections $\sigma_i(E)$ at each photon energy were averaged, and the random experimental error was estimated from the standard deviation of the mean.

The total error reported for each single energy ionization cross section in Table 4 was determined for each species i by summing all errors in quadrature. The dominant source of the error in the absolute cross sections of CH₃OH, HO₂, H₂O₂, and H₂CO reported in Table 4 is the uncertainty in the cross section of the reference compound propene. The uncertainty in the ratio of these cross sections relative to the reported cross section of methanol is actually quite low; therefore, our estimates of the cross sections could be improved by a more precise determination of the methanol cross section.

4. DISCUSSION

4.1. H₂CO. Formaldehyde has been the subject of many VUV studies due to its fundamental importance, as well as its central role in astrochemistry (it was the first organic molecule discovered in the interstellar medium),67 combustion, and atmospheric science.^{36,68-84} The first band (AIE = 10.889 eV),³⁶ which arises from the removal of an electron from the nonbonding 2b₂ oxygen lone pair orbital, consists of a strong origin band followed by a low-intensity vibrational progression.

Two studies have reported the relative photoionization spectrum of H_2CO in the ionization onset region at high resolution.^{73,75} These spectra have a sharp onset at threshold, Article

yielding an AIE = 10.88 eV, consistent with the photoelectron results. Two studies reported low-resolution absolute VUV photoionization cross sections in this region.^{81,83} Cooper et al.⁸¹ determined the absolute H₂CO photoionization cross section using dipole (e,e + ion) coincidence spectroscopy. In these experiments, they first measured absolute total absorption oscillator strengths from electron scattering experiments and then derived partial differential photoionization oscillator strengths from the coincident mass spectrometry measurements. The energy resolution was 1 eV fwhm. The cross sections obtained after deconvolving for the resolution (triangles) is shown in Figure 5a. Theoretical work reproduces the Cooper absolute photoionization spectrum from 18-100 eV but tends to overestimate the threshold region cross section at energies lower than 18 $\mathrm{eV.}^{82,84}$

FitzPatrick et al.⁸³ measured the photoionization cross section of formaldehyde relative to that of the vinyl radical (C_2H_3) in a molecular beam experiment on the 193 nm photodissociation of epichlorohydrin. They assigned formaldehyde and vinyl radicals as products in a 1:1 ratio from the unimolecular decomposition of the C3H5O intermediate. The experiments were conducted under collisionless conditions using photofragment translational spectroscopy to resolve the velocity and angular distributions of the products. The products were photoionized by VUV radiation generated on the 21A1 U9/Chemical Dynamics Beamline at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The spectral



Figure 5. Absolute photoionization spectrum of formaldehyde. Panel a demonstrates the energy-dependent scan reported in this work, scaled to match the absolute photoionization cross sections determined in single energy experiments. The dark gray shading indicates the systematic error from the 2% error in [H₂CO] propagated from the kinetics model. The light gray shading is the total systematic error, including both the error in the kinetics model and the error in the reference methanol cross section. Data taken from Cooper et al.⁸¹ have been deconvolved to match our energy resolution and are plotted here (triangles). Data taken from FitzPatrick et al.⁸³ have been corrected with the new C2H3 measurement, have been deconvolved to match our energy resolution, and are plotted here (squares). Interferences caused by Ar resonances are indicated by asterisks. Panel b compares the experimental rise at threshold with literature high-resolution relative H₂CO spectra. Data (diamonds) are taken from Mentall et al.⁷³ and scaled to match experiment. Data are also shown (triangles) from Guyon et al.⁷⁵ and scaled to match experiment. The AIE is indicated for reference.³

resolution ($\Delta E/E$) was 0.4 at 11.27 eV. FitzPatrick et al. scaled their vinyl spectrum to match a preliminary absolute spectrum from unpublished data by Taatjes ($\sigma_{\text{vinyl}}(10.43 \text{ eV}) = 12.0 \text{ Mb}$) (while noting some difference from prior work by Robinson et al.²³) and determined a photoionization cross section of 4.23 Mb for formaldehyde at 11.27 eV. However, Savee et al. recently reported an absolute photoionization spectrum of C_2H_3 measured with the present MPIMS apparatus (the final analysis of the preliminary cross section reported by Taatjes) that has a significantly lower cross section ($\sigma_{\text{vinyl}}(10.424 \text{ eV}) =$ 8.3 Mb), suggesting an even smaller cross section for formaldehyde in the work of FitzPatrick et al.³¹ In Figure 5a, we show their cross sections reevaluated using Savee's new vinyl cross section and corrected for their spectral resolution (squares).



Figure 6. Absolute photoionization spectrum of HO₂. Energydependent scan in this work, scaled to match the absolute photoionization cross sections determined in single energy experiments. The dark gray shading indicates the systematic error from the 8% error $[HO_2]$ from the kinetics model. The light gray shading is the total systematic error, including both the error in the kinetics model and the error in the reference cross section. The red line is taken from Litorja and Ruscic, arbitrarily scaled to compare the shape with this study.³⁸ The AIE is indicated for reference.³⁸ Interferences caused by Ar resonances are indicated by asterisks.



Figure 7. Absolute photoionization spectrum of H_2O_2 . Energydependent scan in this work, scaled to match the absolute photoionization cross sections determined in single energy experiments. The dark gray shading indicates the systematic error from the 12% error $[H_2O_2]$ from the kinetics model. The light gray shading is the total systematic error, including both the error in the kinetics model and the error in the reference cross section. The red line is taken from Litorja and Ruscic, arbitrarily scaled to compare the shape with this study.³⁸ The AIE is indicated for reference.³⁸ Interferences caused by Ar resonances are indicated by asterisks.

In Figure 5a we compare our experimental H_2CO absolute photoionization spectrum with that of Cooper et al. and FitzPatrick et al. We are in reasonable agreement with the measurements by Cooper et al., but our measurements are a factor of 2 larger than those by FitzPatrick et al.

As seen in Figure Sb, the energy dependence of our spectrum in the threshold region (below 11.2 eV) matches the higher resolution relative spectra of Mentall et al.⁷³ (resolution 0.5 Å (0.5 meV at 11 eV)) and Guyon et al.⁷⁵ (resolution half-width 0.83 Å (0.9 meV at 11 eV)). All three spectra are similar in the threshold region, although our lower resolution spectrum does not capture resonances in the 10.9 eV region. Above ~11.2 eV,

the spectrum of Guyon et al. is independent of energy, whereas our spectrum increases slowly with photon energy. This discrepancy might be due to different strategies to normalize ion signal to the photon flux.

4.2. HO₂. The HO₂ first ionization potential corresponds to removal of an electron from the antibonding combination of the oxygen $2p\pi$ orbitals in the neutral ²A" to form the ³A" cation. There have been several previous studies of the ionization of the HO₂ radical.^{38,85–87} Early electron ionization studies^{85,86} determined the adiabatic ionization potential to be 11.53 eV. In 1981, Dyke et al.⁸⁷ reported a low-resolution photoelectron spectrum of HO₂ and assigned a progression of 1560 cm⁻¹ to v_{2} , the O–O stretch mode in HO₂⁺. Litorja and Ruscic measured the relative photoionization spectrum of HO₂ from 100-111 nm (12.4-11.2 eV) at high resolution (step sizes of 0.02 nm) (shown in Figure 6, scaled to match the absolute cross sections measured here).³⁸ Because the spectrum exhibited a sharp rise at threshold, they could determine the ionization energy of HO₂ with high precision: AIE = $11.352 \pm$ 0.007 eV. There is very good agreement in the shape of our spectrum and that of Litorja and Ruscic, including the positions of the $\nu' = 0$ and 1 steps in the underlying staircase structure caused by the O–O stretch vibrational progression.

Prior to this study, there were no reports of the absolute photoionization cross section of HO₂. One study measured the HO₂ photoionization cross section relative to the photoionization cross section of the methyl peroxy radical, CH_3O_2 , at two photon energies (the Ar resonance lines 11.62 and 11.83 eV) and estimated the HO₂ cross section to be about 5 times lower.⁸⁸ Although the relative photoionization spectrum of CH_3O_2 has been reported,¹⁴ there are no absolute cross sections for CH_3O_2 (and therefore HO_2) with which to compare our results.

4.3. H_2O_2 . There have been a number of photoelectron and photoionization studies of H_2O_2 . The AIE is well-established (AIE = 10.631 ± 0.007 eV).³⁸ The first broad band in the photoelectron spectrum corresponds to removal of an electron from the antisymmetric combinations of oxygen nonbonding orbitals, which have some antibonding character. The dihedral angle significantly increases upon ionization from 120° in the neutral to *trans* planar (180°, C_{2h}) in the cation.^{89–92} Litorja and Ruscic³⁸ reported the only relative photoionization spectrum of H_2O_2 (shown in Figure 7, scaled arbitrarily to match our spectrum). The very gradual rise after threshold is consistent with an extended Franck–Condon envelope resulting from a large geometry change between the neutral and cation.

The relative photoionization spectrum of H_2O_2 reported here is in good agreement with past work by Litorja and Ruscic (Figure 7). There have been no reports of the photoionization cross section of H_2O_2 in the VUV with which to compare our absolute cross sections.

4.4. Validity of Empirical Estimates of Cross Sections. Bobeldijk et al. developed a semiempirical model for estimating the photoionization cross section for closed shell molecules like $H_2CO.^{93}$ The calculated value for H_2CO at 11.8 eV using this model is 13 Mb. Our experimental spectrum above 11.6 eV is noisy, because there are resonances in the spectrum of the Ar gas filter, but the mean cross section from 11.6–12 eV is 14.9 Mb (Table 5) and agrees reasonably with the model. Note that the Bobeldijk et al.⁹³ method does not provide a means to estimate either the HO₂ or the H_2O_2 cross sections.

Because HO₂ and H₂O₂ exhibit very similar HOMOs (Supporting Information) they might serve as a novel test of Xu and Pratt's method²⁸ for estimating photoionization cross sections for free radicals. In short, this model suggests that the cross section for photoionization from the HOMO of a free radical can be estimated by using the cross section for photoionization from an orbital of similar shape on a corresponding closed-shell species. This method also requires scaling the estimated cross section value by the orbital occupancies. A proper comparison should be performed after the Franck-Condon envelope associated with each molecular orbital, although this is not possible in the threshold region of H_2O_2 due to overlapping transitions to multiple electronic states. However, it is qualitatively clear that the near-threshold photoionization cross section of HO₂ is roughly half that of H_2O_{21} as expected from the single vs double occupancy of the HOMOs in these two molecules.

5. CONCLUSIONS

We report absolute VUV photoionization cross sections for HO_2 , H_2O_2 , and H_2CO derived from measurements relative to the photoionization cross section of methanol. The key to this approach has been to obtain concentrations of all species from detailed kinetics modeling of all primary and secondary reactions occurring in the chlorine-initiated oxidation of methanol. Initial radical concentrations were derived from accurate measurements of precursor depletion. The current results are a significant improvement over previous measurements of the absolute cross section of H_2CO , which were recorded at much lower resolution. These represent the first measurements of the HO_2 and H_2O_2 absolute cross sections.

The largest source of error stems from the 20% uncertainty in determining cross sections relative to propene.^{65,66} The precision of the HO₂, H₂O₂, and H₂CO cross sections relative to that of CH₃OH is much higher; hence the absolute cross sections could be improved by better measurements of propene or CH₃OH.

With our measurement of the HO_2 photoionization spectrum, it may be possible to infer the absolute cross section of CH_3O_2 based on the relative relationship provided by Imamura and Washida.⁸⁸ If the HO_2 cross section at 11.62 and 11.83 eV is approximately 5 times lower than that of CH_3O_2 , then the estimated CH_3O_2 cross sections at these energies would be 15.2 and 22.5 Mb, respectively.

 HO_{2} , H_2O_2 , and H_2CO are important in a number of oxidation processes. The cross sections measured here will aid in quantifying concentrations of these species in photo-ionization mass spectrometry studies of combustion and atmospheric chemistry reactions.

ASSOCIATED CONTENT

Supporting Information

Details of the characterization of instruments using NO₂ photolysis; the instrument response function and photolysis gradient; deconvolution procedures; measurement of the methanol photoionization spectrum; examples of additional data; comparison of the HO_2/H_2O_2 HOMOs, and the full kinetics model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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ABBREVIATIONS

OA-TOF, orthogonal acceleration time-of-flight; m/z, mass-tocharge ratio; MPIMS, Multiplexed Photoionization Mass Spectrometer; VUV, vacuum ultraviolet; ALS, Advanced Light Source; IRF, instrument response function; AIE, adiabatic ionization energy

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