



# Absolute photoionization cross-sections of some combustion intermediates

Bin Yang<sup>a</sup>, Juan Wang<sup>a</sup>, Terrill A. Cool<sup>a,\*</sup>, Nils Hansen<sup>b</sup>, Scott Skeen<sup>b</sup>, David L. Osborn<sup>b</sup>

<sup>a</sup> School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA

<sup>b</sup> Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA

## ARTICLE INFO

### Article history:

Received 12 August 2011

Received in revised form 8 September 2011

Accepted 8 September 2011

Available online 16 September 2011

### Keywords:

Photoionization cross-sections

Photodissociation

Photoionization mass spectrometry (PIMS)

Combustion chemistry

Oxygenates

Nitrogenous compounds

## ABSTRACT

Near-threshold absolute photoionization and dissociative photoionization cross-sections for photon energies from 9.7 to 11.75 eV are presented for 30 combustion intermediates including hydrocarbons, oxygenates and nitrogenous compounds (trans-2-butene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, trans-2-hexene, 1-hexene, allene, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,2-butadiene, 1,5-hexadiene, isobutane, methylcyclohexane, furan, 2,3-dihydrofuran, 2,5-dihydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, n-butanal, isobutanal, 2-butanal, 3-methyl-2-butanal, ketene, allyl alcohol, methyl vinyl ketone, dimethoxymethane, methylamine, ethylamine, piperidine). Because allene is one of the most important intermediates in hydrocarbon combustion and pyrolysis processes, very accurate cross-sections for allene are desired to enable the measurement of its mole fractions in flames and to determine relative concentration ratios of allene to its isomer propyne. The cross-sections for allene have thus been re-measured with high precision using an apparatus of improved signal/noise ratio. Furthermore, these allene cross-sections yield accurate previously unmeasured cross-sections for ketene, another key combustion intermediate.

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## 1. Introduction

Benefiting from the development of intense vacuum ultraviolet (VUV) light sources, including synchrotrons, discharge lamps and VUV lasers, single-photon ionization mass spectrometry (PIMS) has recently become increasingly popular for characterizing complex gas-mixtures in chemically reacting systems in atmospheric chemistry, aerosol chemistry, laser-initiated chemical kinetics, low-pressure flames and related processes [1–7]. These PIMS measurements utilize single VUV radiation to photoionize reaction intermediates, products, and photofragments, which are mass-selected and detected. PIMS usually yields substantially less fragmentation upon ionization than electron ionization mass spectrometry (EIMS), and it is particularly useful for those species which cannot be detected by alternative methods such as resonance-enhanced multiphoton ionization or laser-induced fluorescence because of a lack of suitable excited states of the neutral.

Absolute photoionization cross-sections obtained with VUV PIMS are necessary to quantify the concentrations of the species of interest. Because photoionization of a polyatomic species can often result in dissociative ionization within 1–2 eV of the adiabatic ionization energy of the parent molecule, these contributions to the total photoionization cross-sections must be determined. To avoid

the interference between the parent ions of a given mass-to-charge ( $m/z$ ) and ion fragments with the same  $m/z$  derived from other bigger species in a complex system, an accurate determination of mass-resolved partial photoionization cross-sections for parent and dissociative ions are highly desirable for all chemical species probed. Take flame chemistry studies for example; mass-resolved partial cross-sections for combustion intermediates enable species identification through photoionization efficiency (PIE) measurements [3,8,9] and facilitate quantitative determination of mole fractions [10]. Unfortunately, the established photoionization cross section database for hundreds of flames species is far from complete.

Measurement of absolute cross-sections for stable species has been carried out by several different methods. A dual beam single ion chamber [11–14] and a double ion chamber [15–25] are often used to determine the total photoionization cross section through the measurement of the absolute photoabsorption cross section and a determination of the ionization quantum yield. Once the absolute photoionization cross section for one species is known, the absolute photoionization cross-sections for other species can be determined by relative measurements of both species [3,26–34]. Our group has recently determined the absolute photoionization cross-sections for a number of stable combustion intermediates by making relative measurements with respect to propene [3,27,28,35]. More recently, Zhou et al. and Xie et al. [29–32] have measured photoionization cross-sections for a series of compounds with binary-liquid-mixture methods using

\* Corresponding author. Tel.: +1 607 2554191; fax: +1 607 2557658.  
E-mail address: [tacl3@cornell.edu](mailto:tacl3@cornell.edu) (T.A. Cool).

cross-sections for benzene as calibration standards. In addition, absolute photoionization cross-sections for free radicals including methyl [36,37], ethyl [38], vinyl [39], propargyl [39], allyl [40], 2-propenyl [40,41], isopropyl [42], phenyl [43], and formyl [44] have been determined using several different approaches.

In this paper, we present measurements of total and mass-resolved partial photoionization and photodissociation cross-sections for 30 reaction intermediates for photon energies ranging from their respective ionization thresholds up to 11.75 eV. Of particular interest, we present new high accuracy measurements of allene cross-sections using an apparatus of improved signal/noise ratio [3]. These allene cross-sections enable the determination of accurate, previously unmeasured cross-sections for ketene, another key combustion intermediate. The experimental results contribute to a fast growing database of photoionization cross-sections of importance for studies of gas phase chemistry with PIMS.

## 2. Experiments

The experiments described in this paper are performed using a molecular-beam time-of-flight photoionization mass spectrometer. A detailed description of the experimental apparatus and measurement procedures have been provided elsewhere [35]. Briefly, the apparatus consists of a low pressure (ca. 15 Torr) stainless steel sample reservoir, a two-stage differentially pumped molecular beam sampling system, and a 1.3-m linear time-of-flight mass spectrometer (TOFMS) with a mass resolution  $m/\Delta m = 400$ . It is coupled to a 3-m monochromator used to disperse synchrotron radiation at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory [45]. The dispersed photon beam is tunable over the useful range from 8 to 17 eV with a typical energy resolution of 40 meV (fwhm) and photon current of  $5 \times 10^{13}$  photons/s. As in previous studies [35], photoionization cross-sections for target species are determined by calibration of photo-ion signals from the target species against those of propene as a calibration standard with accurately measured photoionization cross-sections over the photon energy range from 9.7 to 11.75 eV [13]. Binary mixtures of a given target molecule with propene are prepared in a 3.8 l stainless steel sample cylinder with a Teflon coated inner surface. Nominal sample mixture compositions consist of 15 Torr each of the target molecule and propene to which 2300 Torr of argon diluent is added. The samples are allowed to mix for at least 8 h and then are introduced as a cold flow to the sample reservoir at a flow rate of 0.12 slm (standard liters per minute) along with a second flow of argon at 0.25 slm. The gas mixture passing from the reservoir with a pressure of 15 Torr expands into the ionization region, where it is crossed by the dispersed VUV light from the monochromator.

Photo-ions extracted by pulse-gating a repeller plate are propelled along the flight tube of the TOFMS and detected by a microchannel plate. Ion counts as a function of ion flight times (15,008 channels of 2 ns bin width) are recorded for  $5 \times 10^5$  to  $2 \times 10^6$  sweeps of a multichannel scaler (Fast ComTek P7886). The resulting mass spectra (ion signal vs  $m/z$ ), obtained from accumulated ion counts integrated over each mass peak, are corrected for background signals and overlapping contributions from  $^{13}\text{C}$  isotopes and finally normalized by the photon current to yield photoionization efficiencies as a function of photon energy (PIE spectra) for both the target molecule and the propene calibration standard.

Absolute photoionization cross-sections for parent ions of the target species are obtained from the PIE spectra for the parent ion and propene with the relationship [35]

$$\sigma_{\text{T}}(E) = \frac{\sigma_{\text{S}}(E)[S_{\text{T}}(E)P_{\text{S}}/S_{\text{S}}(E)P_{\text{T}}]}{R_{\text{T}}/R_{\text{S}}} \quad (1)$$

Here  $\sigma_{\text{T}}(E)$  and  $\sigma_{\text{S}}(E)$  are the respective energy-dependent photoionization cross-sections for the target and standard molecules,  $S_{\text{T}}(E)$  and  $S_{\text{S}}(E)$  are the respective photoionization efficiencies, and  $P_{\text{T}}$  and  $P_{\text{S}}$  are their partial pressures in the sample mixture. The “mass discrimination factor”  $[R_{\text{T}}/R_{\text{S}}]$  for the detection of the target relative to propene is the ratio of the mass-dependent response factors  $R_{\text{T}}$  and  $R_{\text{S}}$  that account for the respective sampling and detection efficiencies for the target and standard molecules [28,35]. For some target molecules with adiabatic ionization energies lower than that of propene, ion signals, corrected for photon current, are used to extrapolate cross-sections to threshold.

Three binary target/propene sample mixtures are independently prepared for each molecule, with the exception of ketene, for which six samples are prepared, and 3-methyl-1-butene, 2,3-dihydrofuran, and 2,5-dihydrofuran, for which 2 samples are prepared. In addition, samples containing only the target molecule with no admixed propene are studied to determine the dissociative ionization cross-sections. In the case of some molecules, a fragment ion for  $m/z=42$  is observed in the absence of admixed propene. The  $m/z=42$  ion signals for the binary target/propene mixtures are corrected to account for this fragment ion contribution.

The sources of the chemicals used in these studies are as follows: propene 99% (Aldrich), trans-2-butene 99+% (Aldrich), 2-methyl-1-butene 98% (Aldrich), 3-methyl-1-butene 95% (Aldrich), 2-methyl-2-butene 99+% (Sigma-Aldrich), trans-2-hexene 97% (Aldrich), 1-hexene 99+% (Aldrich), allene 97% (Aldrich), 1,3-butadiene 99+% (Aldrich), 1,3-pentadiene 98% (Aldrich), 1,4-pentadiene 99% (Aldrich), 3-methyl-1,2-butadiene 97% (Aldrich), 1,5-hexadiene 97% (Aldrich), isobutane 99% (Aldrich), methylcyclohexane 99+% (Sigma-Aldrich), furan 99+% (Aldrich), 2,3-dihydrofuran 99% (Aldrich), 2,5-dihydrofuran 97% (Aldrich), 2-methyltetrahydrofuran 99+% (Sigma-Aldrich), tetrahydropyran 99% (Sigma-Aldrich), butanal 99% (Sigma-Aldrich), isobutanal 99+% (Aldrich), 2-butanal  $\geq 99.5\%$  (Aldrich), 3-methyl-2-butanal 97% (Aldrich), allyl alcohol 98.5% (Aldrich), methyl vinyl ketone 99% (Aldrich), dimethoxymethane 99% (Sigma-Aldrich), methylamine 99.0% (Aldrich), ethylamine 99.0% (Aldrich), piperidine 99.0% (Sigma-Aldrich).

Ketene is not commercially available due to its low boiling point ( $-59.4^\circ\text{C}$ ) and the tendency to polymerize during long storage periods [46]. We synthesize ketene with the procedures reported by Williams and Hurd [47]. Briefly, 100 ml of acetic anhydride is poured into a round bottomed reaction flask. Dry nitrogen enters the reaction flask through a Teflon tube and passes through the apparatus at a flow rate of approximately 1 bubble per 5 s. The acetic anhydride is heated to its boiling point ( $138\text{--}140^\circ\text{C}$ ) using a heating mantle that is placed beneath the round bottomed flask. When the acetic anhydride begins to reflux, a nichrome coil inserted into the reaction flask is heated until it is observed to be a dull red color. The hot metallic coil cracks the acetic anhydride, and forms gaseous ketene. The gaseous ketene and byproducts travel through a water cooled condenser into a first cold trap. This trap, which is cooled using an ice water bath, catches many impurities such as acetic acid. Ketene exits the first trap and travels through a Teflon tube into a final ketene trap. This trap is cooled to 179 K using a liquid nitrogen/hexane slush that is held in a 1 l dewar. A total of 5 ml of ketene is thus synthesized per experiment. The fresh sample of ketene is stored at  $-114^\circ\text{C}$  in a liquid nitrogen/ethanol cooled bubbler. The air in the bubbler is pumped out to yield the pure ketene vapor used to fill the sample cylinders. Nominally 15 Torr ketene, 15 Torr allene and 2300 Torr of argon are combined and allowed to mix for 8 h in a pre-evacuated cylinder before beginning measurements.

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