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PHOTOIONIZATION MASS SPECTROMETRY OF COMBUSTION RADICALS

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Terrill A. Cool, Principal Investigator

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1. J. H. Werner and T. A. Cool., "The Combustion of Trichloroethylene Studied with VUV Photoionization Mass Spectrometry", Twenty-Seventh Symposium (International) on Combustion, The Combustion Institute, (1998), pp. 413-423.

2. J. H. Werner and T. A. Cool, "The Kinetics of the Combustion of Trichloroethylene for Low Cl/H Ratios", Combustion and Flame, in press.

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Abstract

Fundamental research on the combustion of halogenated organic compounds with emphasis on reaction pathways leading to the formation of chlorinated organic compounds and the development of continuous emission monitoring methods will assist in DOE efforts in the management and control of hazardous chemical wastes.

Selective laser ionization techniques are used in our laboratory for the measurement of concentration profiles of radical intermediates in chlorinated hydrocarbon flames. A novel flame-sampling VUV laser photoionization mass spectrometer, constructed with DOE funding, is in use for these studies. Progress is reported here on the use of this new facility in the development, refinement, and verification of chemical kinetic models describing the thermal destruction of toxic chlorocarbons commonly found in chemical wastes.

The use of VUV laser photoionization mass spectrometry for flame species profile measurements has important advantages over other laser-based techniques (LIF, REMPI, laser absorption spectroscopy) and conventional electron-impact ionization mass spectrometry.

- This new approach largely avoids parent ion fragmentation problems, has a sensitivity comparable to LIF and REMPI methods, and requires no prior spectroscopic information.
- Measurements of mass resolved photoionization efficiency (PIE) curves, inherent in this approach, provide a high degree of species selectivity, which is quite important in the complex flame species environment.
- The PIE measurements yield low resolution (± 0.01 eV) estimates of ionization potentials, which are often useful for the identification of structural isomers.

In contrast to the LIF and REMPI methods, VUV laser ionization mass spectrometry may yield *absolute* rather than *relative* species concentration profiles with the use of reliable calibration methods, similar in concept to those currently in use with conventional electron-impact ionization mass spectrometry. Indeed, a major focus of our recent effort has been the development of photoionization efficiency calibrations, needed for accurate absolute determinations of flame species concentrations.

In the past two years we have used the flame sampling VUV laser ionization mass spectrometer system for studies of chlorocarbon-doped methane/oxygen flames. Relative concentration profiles and photoionization efficiency curves have been

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measured for over two-dozen key reaction intermediates. Preliminary kinetic models have been developed that promise an improved understanding of chlorocarbon chemistry under laboratory flame conditions.

I. INTRODUCTION

Public concerns regarding the safety of thermal processing for the destruction of hazardous chemical wastes may be addressed with the development of predictive kinetic models to assist in the design and operation of incinerator facilities. Such kinetic models may provide an understanding of the reaction pathways leading to the formation of chlorinated aromatic compounds and assist in the development of sensitive and selective continuous toxic emissions monitoring techniques.

Thermal processing of hazardous chemical wastes requires that the waste feed stream be exposed to the primary and postflame zones of a hydrocarbon-fueled incinerator. A significant concern is the formation of toxic combustion byproducts when the waste stream contains chlorinated compounds (*e.g.*, industrial solvents, plastics, medical wastes). These toxic byproducts may include chlorinated benzenes, phenols, biphenyls and polycyclic aromatics.

The successful design, operation and monitoring of thermal processing requires a knowledge of the chemical mechanisms by which such toxic byproducts are formed. A predictive kinetic model of chlorocarbon combustion should assist in the selection of appropriate operating conditions and identify key species to be continuously monitored in real time to ensure timely detection of "upset" conditions, which may require combustion adjustments (including system shutdown if necessary).

Although reliable kinetic models exist for hydrogen/oxygen and methane/oxygen combustion, the introduction of chlorocarbons is a significant complication. Many important general features of chlorocarbon combustion are reflected in current models [1-3], but the intricate pathways leading to the formation of chlorinated polycyclic aromatics have not yet been adequately described. Quantitative measurements of radical species concentrations under well-defined laboratory conditions reveal these pathways and provide a means to test and modify postulated reaction mechanisms. The flame-sampling VUV laser ionization mass spectrometer developed in this program is particularly well-suited for studies of radical intermediates because of its sensitivity and selectivity.

II. THE FLAME-SAMPLING VUV LASER IONIZATION MASS SPECTROMETER

In our experiments, small amounts of selected chlorocarbons are introduced to a well-characterized methane/oxygen flame. The presence of chlorocarbons perturbs the composition of the radical pool resident in this standardized flame and produces small concentrations of interesting new reaction intermediates, which are selectively monitored.

Fig. 1 is a schematic diagram of the apparatus. The principal components of this system are a low pressure flame chamber, a differentially pumped flame sampling system, and a laser ionization time-of-flight mass spectrometer (TOFMS). A flat-flame burner with a porous stainless steel head (McKenna Products) with a 6-cm-diameter flame zone and surrounding argon shroud flow is mounted with the flow axis in a horizontal plane. Horizontal mounting allows a vertical alignment of the axis of the time-of-flight mass spectrometer to facilitate cooling of the flight tube wall surfaces with a surrounding liquid nitrogen dewar. Transverse buoyancy effects on the flame are negligible for the low flame pressures (ca 50 torr) of these studies.

Calibrated mass flow controllers (Tylan FC 280) regulate gas flows to the $\text{CH}_4/\text{O}_2/\text{Ar}$ flame with volume flow rates (slm) of 0.75/1.5/2.0. The argon flow is seeded with a small amount (0.085 slm) of TCE, vaporized at room temperature from its liquid, and then mixed with the CH_4 and O_2 flows prior to entering the burner head.

Flame sampling is accomplished with a nickel sampling cone, of 25° half angle and 0.2-mm-diameter orifice, mounted on a water-cooled copper flange, which serves as the end wall of the flame chamber as illustrated in Fig. 1. The distance from the entrance tip of the sampling cone to the mounting surface of the water-cooled copper flange is 27.3 mm; at this distance the flow at the sampling point on the flame axis is quasi-one-dimensional with no recirculation caused by the cooled end wall.

A nickel skimmer with its 2-mm-diameter orifice located 17 mm downstream of the

Figure 1: Flame-sampling laser-ionization TOFMS. A computer controlled translatable flat flame burner is located on the left.

0.2-mm-diameter orifice of the sampling cone, forms the molecular beam, which passes through the acceleration plates of the TOFMS shown in Fig. 1. The horizontally directed, unfocused, VUV laser beam intersects the molecular beam at right angles on the axis of the TOFMS flight tube. The TOFMS is of the classic dual-field Wiley-McLaren design,[7] with an electron multiplier detector (Johnston MM-1) located 1.3 m from the ionization region.

Fig. 2 illustrates the krypton cell used for four wave sum-difference mixing, based on the enhanced nonlinear susceptibility of krypton at a two photon resonance near 212.5 nm.[8,9] Two laser photons of frequency ω_r , tuned to this $5p4p^5 \leftarrow 4p^6$ ($2p_5 \leftarrow 1p_0$) two-photon resonance, are mixed with a third photon of frequency ω_t from a tunable dye laser to generate light at the difference frequency $\omega_{\text{vuv}} = 2\omega_r - \omega_t$. [8,9] A VUV transmitting magnesium fluoride exit window on the krypton cell serves as the vacuum-sealed entrance window to a Pyrex capillary light pipe (4.5 mm i.d.), which guides the light directly to the ionization region of the TOFMS. Approximately 10 nJ of VUV light intersects the molecular beam at a right angle.

A schematic of our laser set-up is shown in Fig. 3. Two dye lasers (Lumonics HD500 and Lambda Physik Scanmate) are pumped by the third harmonic of a 10 Hz Q-switched Nd-YAG laser (Spectra Physics GCR6). Each laser is pumped with approximately 180 mJ of this 355 nm light. The output of the Scanmate (20 mJ at 425 nm) is doubled in BBO to generate about 2 mJ of the requisite 212.5 nm light at ω_r . This laser's frequency is monitored and controlled by directing a small fraction of its

Figure 2: Apparatus (top view) showing krypton frequency mixing cell.

Figure 3: Tunable VUV laser system.

output beam to a Kr cell equipped with a voltage probe designed to detect the resonant three photon ionization ($2+1$ REMPI) signal at 212.5 nm. The tunable output pulse of the tunable dye laser (ca 10 mJ for the 455-475 nm range and ca 16 mJ from 500-530 nm) is delayed to ensure good temporal overlap with the 212.5 nm laser pulse. A pulsed wavemeter (Burleigh WA 4500) provides wavelength calibration of this tunable dye laser to an accuracy of ± 0.001 nm. A dichroic beam splitter with high reflectivity at 212.5 nm enables overlapping of the two laser beams. Once overlapped, the beams pass through a 30 cm focal length lens and into a cell filled with about 20 torr of krypton. A set of two 50 cm lenses, placed in the delay line of the tunable beam, control the beam divergence to ensure that both beams come to a focus at the same place inside the krypton cell.

III. RESULTS

Accurate flame temperature profiles are needed for successful flame modeling. Our approach is to use fine 0.005-in Pt/Pt-13%Rh thermocouples with a Y_2O_3/BeO anticatalytic coating, carefully corrected for radiative cooling. The radiative cooling corrections are based on sodium-line-reversal (SLR) measurements of the true flame temperatures corresponding to each of several thermocouple temperatures throughout the flame zone.[10] Temperature profiles obtained for $CH_4/O_2/Ar$ and $CH_4/TCE/O_2/Ar$ flames are displayed in Fig. 4. Each temperature measurement has an estimated uncertainty of ± 50 K.

A weak secondary source of ionization caused by the acceleration of

Figure 4: Temperature Profiles

Figure 5: Partial TOFMS ion spectrum.

photoelectrons produced by the VUV beam[11-14] was quite helpful for the detection of major flame species (CH_4 , H_2O , HCl , CO , CO_2 , O_2 , Ar) with ionization potentials above the 8.2-10.0 eV energies of the tunable VUV laser. Ion masses of several of these species are indicated in the mass spectrum displayed in Fig. 5. Also shown in Fig. 5 are radical intermediates (C_2H_3 , HCO , C_3H_3 , C_3H_5) directly ionized by the VUV, typically present in concentrations 10^{-3} to 10^{-4} below those of the major species.

Fig. 6 displays mass peaks for dichloroketene and dichloroethenol produced with a photon energy of 10.5 eV (obtained by tripling the Nd-YAG third harmonic in a xenon cell), well above their respective ionization thresholds of 9.15 and 9.08 eV. The $^{35}\text{Cl}^{37}\text{Cl}$ dichloroketene isotopomer of $m/z = 112$ overlaps the $^{35}\text{Cl}^{35}\text{Cl}$ isotopomer of dichloroethenol at this photon energy. By reducing the ionization energy to 9.12 eV, just below the threshold for ionization of dichloroketene, all three ($^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$, $^{37}\text{Cl}^{37}\text{Cl}$) isotopomers of dichloroethenol appear separately with relative signals corresponding to their respective isotopic abundances, as shown in Fig. 7. Figs. 6 and 7 illustrate the importance of the proper choice of VUV wavelength for monitoring the concentration of a given species. Indeed, as is discussed in Section III-B, measurement of the PIE curve often provides an unambiguous identification of one of several possible structural isomers.

A. Relative Concentration Profiles

A series of time-of-flight mass spectra, taken for each of several positions of the sampling cone relative to the burner face, and recorded for a number of different photon energies spanning the

Figure 6: Partial TOFMS ion spectrum for dichloroketene and dichloroethenol.

The $^{35}\text{Cl}^{37}\text{Cl}$ dichloroketene isotopomer of $m/z = 112$ overlaps the $^{35}\text{Cl}^{35}\text{Cl}$ isotopomer of dichloroethenol at this photon energy. By reducing the ionization energy to 9.12 eV, just below the threshold for ionization of dichloroketene,

all three ($^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$, $^{37}\text{Cl}^{37}\text{Cl}$) isotopomers of dichloroethenol appear separately with relative signals corresponding to their respective isotopic abundances, as shown in Fig. 7. Figs. 6 and 7 illustrate the importance of the proper choice of VUV wavelength for monitoring the concentration of a given species. Indeed, as is discussed in Section III-B, measurement of the PIE curve often provides an unambiguous identification of one of several possible structural isomers.

Figure 7: TOFMS ion spectrum for dichloroethenol.

range from 8.2 to 10.5 eV have been used to determine relative flame concentration profiles for the 28 flame species listed in Tables I-IV. Several of these profiles are compared with preliminary model calculations (discussed in Section V-D) in Figs. 8-20.

The calculated concentration profiles have been uniformly shifted by 0.85 mm toward the burner to compensate for the fact that the sampling cone draws from a flame region extending several orifice diameters ahead of the cone [15,16]. Each of the relative concentration profiles have been scaled vertically to match the calculated curves. In future work (described in Section V-A) we hope to determine the ionization cross sections for each species so that the data may be placed on an absolute scale without reference to the calculated curves. The relative concentration profiles for the major species (TCE, CH_4 , H_2O , HCl , CO , CO_2 , O_2) shown in Figs. 8-10 are in excellent agreement with the calculated profiles; this good agreement provides justification for the 0.85 mm shift between measured and calculated profiles.

Relative concentration profiles for a number of stable species (chloroethylenes, chloroketenes, dichloroethanol, and several hydrocarbons) and radical intermediates (CH_3 , CH_2Cl , HCO , C_3H_3) detected by direct VUV photoionization are also compared with preliminary model calculations in Figs. 11 to 20. Each profile has a shape in good qualitative agreement with the model calculations, but until the ionization cross section data are available to place measured concentrations on an absolute scale, we have no means to determine the accuracy of the predicted peak concentrations for each species. Indeed, because the peak concentration values are quite sensitive to the rate constant values used in the model, absolute concentration measurements are crucial in evaluation of the validity of the model calculations.

A literature search of available photoionization cross sections for alkenes, alkynes, and alkanes suggests that when the first and second ionization potentials are separated by 1.5-2 eV or more (as in most alkenes), the cross sections typically display a plateau at energies between the first and second ionization limits. [17-22] Cross section values at the plateau range from about 8-10 Mb ($1\text{ Mb} = 10^{-18}\text{ cm}^2$) for alkenes and 20-30 Mb for alkynes. It is our intent to measure ionization cross sections for all of the stable species detected in these experiments and develop semi-empirical cross section

Figure 8: Relative concentration profile for trichloroethylene.

Figure 9: Relative concentration profiles for H_2O , CH_4 , and HCl .

Figure 10: Relative concentration profiles for O_2 , CO , and CO_2 .

Figure 11: Relative concentration profiles for 1,1-DCE, vinyl chloride, and ethylene.

Figure 12: Relative concentration profiles for ketene, chloroketene, and dichloroketene.

Figure 13: Relative concentration profile for dichloroethanol.

Figure 14: Relative concentration profile for 1,3-butadiene.

Figure 15: Relative concentration profile for vinyl acetylene.

Figure 16: Relative concentration profile for benzene.

Figure 17: Relative concentration profile for HCO.

Figure 18: Relative concentration profile for CH_3 .

Figure 19: Relative concentration profile for CH_2Cl .

Figure 20: Relative concentration profile for the propargyl radical.

TABLE I:

Stable Species Detected

Detection via Electron Impact

Species	Relative Cross Section
CH ₄ Methane	0.002
O ₂ Oxygen	0.0008
H ₂ O Water	0.001
CO Carbon Monoxide	0.0012
CO ₂ Carbon Dioxide	0.0004
HCl Hydrochloric Acid	0.0006
Ar Argon	0.001

TABLE II:

Stable C₂ Species Detected

Detection via VUV

Species	Relative Cross Section
Trichloroethylene	10
1,1-Dichloroethylene	26
Vinylchloride	10
Ethene	22
Dichloroethanol	3.4
Dichloroethene	130
Chloroethene	220
Ketene	4100

TABLE III:

Radical Species Detected

Species	Relative X-Section	Method
CH_3 Methyl	12	VUV
HCO Formyl	11	VUV
CH_2Cl Chloro Methyl Radical	13	VUV
C_2H_3 Vinyl	0.20	VUV
$\text{H}-\text{C}(\text{Cl})=\text{C}(\text{Cl})\cdot$ Dichlorovinyl Radical	0.088	VUV
$\text{CH}_2=\text{CH}\cdot$ Propargyl	1.0	VUV
$\text{CH}_2=\text{CH}-\text{CH}_2\cdot$ C_3H_5	5.0	VUV
$\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)\cdot$ C_4H_7		VUV

TABLE IV:

Stable $\text{C}_4 - \text{C}_6$ Species Detected

Species	Relative X-Section	Method
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ Vinyl Acetylene C_4H_4	830	VUV
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-Butadiene C_4H_6	670	VUV
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$ 3-Penten-1-yne C_5H_6		VUV
C_5H_8		VUV
C_6H_6 Benzene	2.8	VUV

estimation methods for radical species (see Section V-B), but in the absence of these data it is reasonable to assume that the ionization cross sections in the plateau region for the molecules of present interest are about 10 Mb, to within a factor of two.

To illustrate the differences between the ionization efficiencies for species detected by direct VUV photoionization and those detected by laser-induced electron impact ionization, a "relative cross section" has been assigned to each of the species listed in Tables I-IV. This "relative cross section" is proportional to the ratio of the measured ion signal strength divided by the calculated species peak mol fraction. The constant of proportionality has been assigned by assuming that the relative cross section for trichloroethylene is 10 Mb.

Comparison of the relative cross section values of Tables I-IV reveals several interesting relationships:

1. The relative cross sections for laser induced electron impact ionization are typically smaller than those for direct VUV photoionization by a factor of about 10^{-3} .
2. The relative cross sections for CH_3 , HCO , CH_2Cl , the chloroethylenes and dichloroethenol are indeed close to 10 Mb, ranging from 3.4 to 26 Mb. These values suggest that the predicted peak mol fractions are quite reasonable at this stage of our model development.
3. The much larger relative cross sections for the ketenes and many of the C_3 - C_5 hydrocarbons indicates that the peak mol fractions for these molecules are underpredicted by the present model.
4. The very small relative cross sections for the vinyl and dichlorovinyl radicals suggest that the concentrations of these important radicals are seriously overpredicted by the present model.

B. Photoionization Efficiencies

A major advantage of VUV laser photoionization over conventional electron impact photoionization is the selectivity provided by mass resolved measurements of photoionization efficiency curves for each species of interest. Often structural isomers have measurably different ionization potentials and thus the structure of a species at a given m/z value may be determined from measurements of its photoionization threshold energy.

A knowledge of the photoionization threshold also makes it possible to monitor a given species with a photon energy sufficiently close to its threshold to ensure that the appearance of a given ion is not associated with the fragmentation of a parent species.

This applies to the majority of cases for which daughter ions have ionization energies below that of the parent ion. In some cases, however, a potential fragment species may have a somewhat higher ionization potential than that of its parent and problems may be encountered. In our experiments such "problem" species include Cl, O, H, OH, C₂Cl₂, and HCl.

The photoionization efficiency curve for the CH₃ radical is shown in Fig. 21. In this case a sharply defined ionization threshold owes its existence to the fact that the structures of the neutral CH₃ and cation CH₃⁺ are very similar with vertically displaced potential energy surface minima. In this situation the apparent ionization threshold may be estimated by the departure from linearity on the semilogarithmic graph of Fig. 22, indicated by the intersection of the two solid lines. This intersection occurs at 9.83 ± 0.01 eV. In the presence of the 180 V/cm draw-out DC electric field in the ionization region of the TOFMS, field ionization of Rydberg states[23,24] lying within approximately $6.1\sqrt{180} = 81$ cm⁻¹ (0.01 eV) of the true ionization threshold may contribute to the observed ionization signal. With this correction the ionization potential for CH₃ is thus placed at 9.84 ± 0.01 eV in excellent agreement with its known value.[25]

A similar sharp ionization threshold is observed for C₂H₂Cl₂ at $m/z = 96$, displayed on the semilogarithmic plot of Fig. 23. An ionization threshold of 9.83 ± 0.01 eV, after correction for Rydberg state ionization, is obtained, which agrees well with the known ionization potential for 1,1-dichloroethylene. Because the ionization potentials for the *cis* and *trans* isomers are known to be about 9.65 ± 0.01 eV, these species are eliminated as

Figure 21: Photoionization efficiency curve for CH₃

Figure 22: Semilogarithmic PIE curve for CH₃.

candidates for the $m/z = 96$ signal. The fact that only 1,1-DCE is observed provides a useful clue to the mechanism by which 1,1-DCE is formed. Indeed, this observation is consistent with the conclusion of Tsang and Walker[26] that H-atom addition followed by Cl-atom elimination dominates abstraction of Cl by H for chloroethylenes at the flame temperatures of interest here. 1,1-DCE is formed when an H atom addition and Cl elimination occurs at the carbon site on the H-atom end of trichloroethylene.

In contrast to the photoionization efficiency curves for CH_3 and 1,1-DCE, a PIE curve with a slowly increasing linear variation above threshold is observed for $m/z = 112$ as shown in Fig. 24. In this case an accurate determination of the ionization threshold would require a knowledge of the vibronic wavefunctions for neutral and cation to account for the unresolved structure responsible for the gradually rising PIE curve. The fact that signals at both $m/z = 112$ and $m/z = 114$ exhibit similar PIE curves and that these signals have strengths consistent with the relative isotopic abundances of $^{35}\text{Cl}^{35}\text{Cl}$ and $^{35}\text{Cl}^{37}\text{Cl}$ isotopomers suggests that these signals correspond to dichloroethenol $\text{C}_2\text{H}_2\text{OCl}_2$ with the structure

suggested by Kirchner, *et al.*, [27] formed by OH addition to and Cl elimination from trichloroethylene. Here again the addition/elimination displacement channel dominates the possible abstraction of an H atom by OH. Although the low resolution of our measurements restricts the accuracy of

Figure 23: Semilogarithmic PIE curve for 1,1-DCE.

Figure 24: Photoionization efficiency curve for dichloroethenol.

threshold determinations, we estimate the ionization potential of dichloroethanol to be 9.08 ± 0.02 eV from the data of Fig. 24. This estimate is obtained by a linear extrapolation of the PIE curve to the baseline at 9.05 ± 0.02 eV, to which we add 0.02 eV to account for internal excitation effects at the rotational temperature ($T \leq 160\text{K}$) of the molecular beam, and an additional 0.01 eV to account for Rydberg state field ionization. Two other structural isomers of $\text{C}_2\text{H}_2\text{OCl}_2$, dichloroacetaldehyde and chloroacetylchloride (cf. Fig. 25), have respective ionization potentials of 10.5 and 11.0 eV, but no previous measurements of the ionization potential of dichloroethanol are available.

Table V summarizes the threshold ionization energies we have obtained from the PIE curves for a number of flame species. In every case the threshold energies are in very good agreement with precise values taken from the literature. Although the thresholds determined from the PIE curves are of limited accuracy (± 0.01 - 0.02 eV) compared with those measured spectroscopically with various techniques (*e.g.*, PES, REMPI, ZEKE, MATI, PIRI), they are nonetheless quite useful for species identification. In some cases the flame zone may be a convenient source of new radical species for which no previous ionization potential measurements exist; the PIE curves may then be expected to yield approximate (± 0.02 eV) values, which may provide a convenient reference for more precise studies.

IV. SUMMARY OF COMPLETED WORK

In our work to date we have demonstrated that flame-sampling VUV laser photoionization mass spectrometry is a valuable new method for recording relative concentration profiles for reaction intermediates in laboratory flames. The method offers several advantages:

3 Isomers of $\text{C}_2\text{H}_2\text{OCl}_2$

Dichloroethanol

$$\Delta H_f^\circ = -38 \text{ kcal/mol (group additivity estimate)}$$

$$\text{I.P.} = 9.08 \pm 0.02 \text{ eV (This work)}$$

Dichloroacetaldehyde

$$\Delta H_f^\circ = -43 \pm 5 \text{ kcal/mol (measured)}$$

$$\text{I.P.} = 10.5 \text{ eV (Literature)}$$

Chloroacetylchloride

$$\Delta H_f^\circ = -59 \pm 2 \text{ kcal/mol (measured)}$$

$$\text{I.P.} = 11.0 \text{ eV (Literature)}$$

Figure 25: Three isomers of $\text{C}_2\text{H}_2\text{OCl}_2$.

TABLE V:

Ionization Potentials

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Species	Ionization Potential (eV)	
	This work	Literature
CH_3	9.84 ± 0.01	9.84 ± 0.01
9.48 ± 0.02	9.47 ± 0.01
9.83 ± 0.01	9.79 ± 0.04
9.08 ± 0.02	Not previously measured
9.15 ± 0.01	9.15 ± 0.01
9.22 ± 0.01	9.24 ± 0.01
9.05 ± 0.02	9.07 ± 0.01
9.14 ± 0.01	9.14 ± 0.04
CH_2Cl	8.88 ± 0.01	8.87 ± 0.01
CHCl_2	8.55 ± 0.01	8.54 ± 0.01

1. A sub-ppm detection sensitivity is achieved (similar to that of REMPI or LIF).
2. Mass-resolved measurements of photoionization efficiencies are an integral part of the technique. These measurements ensure selective detection of a given species present in a complex background of other flame species.
3. This approach largely avoids fragmentation problems common to conventional electron-impact mass spectrometry. In exceptional cases (O, H, OH, Cl, C₂Cl₂, HCl) target species have ionization potentials that exceed those of potential precursor parent species, and difficulties are encountered with either approach.
4. This method is versatile. No prior spectroscopic information is required for species detection and identification. Three types of ionization may be used in the same apparatus. Besides direct single photon VUV photoionization, both REMPI and laser-induced electron impact ionization may be employed.
5. The technique is convenient for low resolution (± 0.01 - 0.02 eV) measurements of ionization potentials of radical intermediates. In many cases these measurements are useful in making species identifications (*e.g.*, species with similar or identical m/z values).

A major goal of our research is the development of useful kinetic models of the combustion of a few selected chlorocarbons (trichloroethylene, chloroform, methyl chloride) with particular emphasis on precursor pathways that lead to the formation of toxic combustion byproducts. The identification of reaction intermediates and quantitative determinations of their concentration profiles in well-defined laboratory flames are essential inputs to this model development effort.

The Appendices to this report present detailed results obtained for the chemistry of flames containing trichloroethylene, during the final year of this program. These results are contained in the two papers:

1. J. H. Werner and T. A. Cool., "The Combustion of Trichloroethylene Studied with VUV Photoionization Mass Spectrometry", Twenty-Seventh Symposium (International) on Combustion, The Combustion Institute, (1998), pp. 413-423.
2. J. H. Werner and T. A. Cool, "The Kinetics of the Combustion of Trichloroethylene for Low Cl/H Ratios", Combustion and Flame, in press.

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V. PUBLICATIONS OF DOE SUPPORTED RESEARCH

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1. N. Hemmi and T. A. Cool, "Magnetic Modulation of Hyperfine Quantum Beats", *J. Chem. Phys.* **102**, 1867 (1995).
2. S. Satyapal, J. H. Werner, and T. A. Cool, "An Extended Flame Zone in the Combustion of CH_3Cl ", *Combust. Sci. Tech.* **106**, 229 (1995).
3. T. A. Cool and N. Hemmi, "Hyperfine Polarization Quantum Beats in Cyanogen", *J. Chem. Phys.* **103**, 3357 (1995).
4. N. Hemmi and T. A. Cool, "Quantum Beats in Cyanogen from Singlet/Singlet and Singlet/Triplet Superposition States", *J. Chem. Phys.* **104**, 5721 (1996).
5. N. Hemmi and T. A. Cool, "Hyperfine Quantum Beats in the 209 nm Fluorescence Excitation Spectrum of Cyanogen", *J. Chem. Phys.* **105**, 7964 (1996).
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8. J. Velazquez and T. A. Cool, "Resonance Ionization Spectroscopy of Cyanogen", *J. Chem. Phys.*, **108**, 3458 (1998).
9. J. Velazquez, L. A. Voloboueva, and T. A. Cool, "Selective Detection of Dibenzodioxin, Dibenzofuran and Some Small Polycyclic Aromatics", *Combustion Science and Technology*, **134**, 139 (1998).
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11. J. H. Werner and T. A. Cool., "The Combustion of Trichloroethylene Studied with VUV Photoionization Mass Spectrometry", *Twenty-Seventh Symposium (International) on Combustion*, The Combustion Institute (1998), pp. 413-423.
12. J. H. Werner and T. A. Cool, "The Kinetics of the Combustion of Trichloroethylene for Low Cl/H Ratios", *Combustion and Flame*, in press.
13. N. Hemmi, "Hyperfine Quantum Beats in Cyanogen", Ph.D. Thesis, Cornell University, August, 1996.

14. J. Velazquez, "Detection Limits of Aromatic Hydrocarbons and Ultraviolet Spectroscopy of the Cyanogen Molecule Using Resonance-Enhanced Multiphoton Ionization", Ph.D. Thesis, Cornell University, August, 1996.
15. J. H. Werner, "VUV Laser Photoionization Studies of Selected Flames", Ph.D. Thesis, Cornell University, January, 1998.

VI. APPENDICES (two recent publications)

1. J. H. Werner and T. A. Cool., "The Combustion of Trichloroethylene Studied with VUV Photoionization Mass Spectrometry", Twenty-Seventh Symposium (International) on Combustion, The Combustion Institute, (1998), pp. 413-423.
2. J. H. Werner and T. A. Cool, "The Kinetics of the Combustion of Trichloroethylene for Low Cl/H Ratios", Combustion and Flame, in press.

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