MASS RESOLVED RESONANCE IONIZATION SPECTROSCOPY
OF COMBUSTION RADICALS

CONTENTS

I. SUMMARY ........................................................................................................... 1

II. INTRODUCTION ................................................................................................. 2

III. SUMMARY OF RESEARCH ACCOMPLISHED UNDER THIS GRANT .......... 4

A. REMPI Spectroscopy of HCO and DCO ..................................................... 4

  Experimental ........................................................................................................ 5
  Vibrational Spectra for the $3\pi$ States of HCO and DCO ............................... 6
  Rotational Spectra; Symmetry Assignments ................................................... 9
  The Renner effect ............................................................................................ 12
  REMPI Spectra for the $B^2\Sigma - X^2\Pi$ Band System .................................. 13

B. REMPI Spectroscopy of the Ethynyl Radical .............................................. 16

C. REMPI Spectroscopy of New Electronic States of $C_2$ ............................... 17

  Observed Spectra ........................................................................................... 18

D. A Flame Sampling Laser Ionization Mass Spectrometer ............................. 19

IV. CONTINUED RESEARCH PLANS .................................................................... 22

A. The Use of REMPI for Monitoring Radical Intermediates ......................... 23

B. The Flame Sampling Laser Ionization Mass Spectrometer ......................... 25

  Experimental Approach ................................................................................ 26

BIBLIOGRAPHY ...................................................................................................... 28

PUBLICATIONS DESCRIBING GRANT SUPPORTED RESEARCH ................. 35

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J. SUMMARY

The capabilities of resonance-enhanced multiphoton ionization (REMPI) spectroscopy for the quantitative detection of trace species may provide solutions to two problems of concern to the U.S. Department of Energy. The first of these is the formulation of accurate models of fossil fuel combustion chemistry. REMPI[1-6] and laser-induced fluorescence (LIF) spectroscopy[7-13] are well-suited for in situ flame radical species profile measurements. Such profile measurements, traditionally accomplished with flame sampling mass spectrometry, a more intrusive technique, have served as a keystone for the development and verification of chemical kinetic models of combustion. A second area of immediate concern is the safe disposal of hazardous wastes. REMPI spectroscopy, combined with molecular beam mass spectrometry, has an incomparable sensitivity for the detection of wide classes of organic molecules. Indeed the selective, ultrasensitive (part-per-billion) REMPI detection of many toxic substances commonly present in the effluent of hazardous waste incinerators has been recently demonstrated.[14-18]

The application of the REMPI technique to combustion diagnostics is acutely limited by a present lack of spectroscopic data for key flame radicals. Continued support is requested for REMPI spectroscopic studies of the electronic states of radical species of importance in the combustion of hydrocarbons and chlorinated hydrocarbons. Particular emphasis will be placed on radical intermediates formed in the incineration of chlorinated organic molecules. Because many of these radicals are expected to be only weakly fluorescent, REMPI diagnostics may be the method
of choice for laboratory flame studies directed toward the development and refinement of chemical kinetic flame models.

A summary of research accomplished to date under this research program is presented in Sections II and III; particular emphasis is placed on newly completed and unpublished work on HCO and DCO. This is followed, in Section IV, by a description of proposed studies to be carried out with a new apparatus completed as part of this program during the past year. The new apparatus will enable useful REMPI spectral signatures to be generated for flame radical species with a more efficient approach than that followed to date.

II. INTRODUCTION

Studies of the REMPI spectroscopy of radical intermediates in combustion are supported under this program. REMPI spectral signatures and spectroscopic constants have been obtained for several previously unobserved electronic states in C$_2$, C$_2$H, C$_2$D, HCO and DCO. Our approach has been to employ excimer laser photolysis of an appropriate precursor to obtain the radical species of interest. Molecular beam time-of-flight mass spectrometry provides identification of REMPI ions produced with the tightly focused beam of an excimer or Nd:YAG pumped tunable dye laser. A schematic diagram of the apparatus used for this work is given in Fig. 1.

Once suitable spectral signatures are obtained for a species of interest, it is then possible to make quantitative species profile measurements with a small Langmuir probe inserted within a laboratory flame.[1-6,19] Our flame radical profile
Figure 1: Molecular beam, laser photolysis, TOFMS apparatus in present use for REMPI spectroscopy of selected photofragments. Dye laser 2 is normally pumped by a Nd:YAG laser (not shown). Laser 1 may be doubled; laser 2 may be doubled and mixed measurements, designed for the evaluation of current chemical kinetic flame models, described elsewhere,[3,6] are beyond the scope of the DOE supported work.

This approach has been quite successful for HCO, the radical on which we have focused a major part of our effort. Because there is no a priori certainty that suitable REMPI signatures will be obtained, however, this experimental plan has definite limitations, exemplified by our work on the ethynyl radical C_2H.[20] As it happens, this radical is unsuitable for REMPI flame diagnostics because the spectra for C_2H and C_2D are diffuse and exhibit the effects of strong predissociation.[20]
A more productive approach may be to first ascertain that a radical species of interest yields a sharp REMPI spectrum before undertaking the difficult, time consuming process of generating that species photolytically and then searching for its REMPI signature. For this reason we have designed and assembled a flame sampling laser ionization mass spectrometer. This apparatus will provide mass-resolved REMPI spectra for flame radicals generated in situ.

Section III, below, describes recent unpublished spectroscopic studies of HCO and DCO and briefly summarizes other studies of C$_2$ and C$_2$H accomplished with this grant. Section IV describes studies to be undertaken with the new apparatus and their relevance to combustion science.

III. SUMMARY OF RESEARCH ACCOMPLISHED UNDER THIS GRANT

A. REMPI Spectroscopy of HCO and DCO

REMPI measurements of HCO density profiles in low pressure laboratory flames, coupled with LIF and REMPI measurements of profiles for O, H, OH, CH, CO and CH$_3$ have provided useful comparisons with the predictions of present chemical kinetic modeling codes (Sandia Laboratories CHEMKIN-II and PREMIX).[6] The stoichiometric methane/oxygen flame is well understood, but important problems remain with predicted profiles for flames involving C$_2$ species chemistry. Specifically, HCO concentrations are overpredicted while CH concentrations are underpredicted; the difficulty has been traced to uncertainties in the rate constant and products of the reaction of the vinyl radical with oxygen at temperatures above 600 K.[6]

The spectroscopic basis for these measurements was established by studies of
the (2+1) REMPI of HCO and DCO from 373 to 460 nm performed under this grant, shortly after its inception.[21] The recent availability of the BBO (β-barium borate) frequency doubling crystal has made possible significant additions to the knowledge of the 3p Rydberg[22] and B valence[23-25] states of HCO and DCO. A discussion of our recent unpublished (1+1) REMPI measurements[22,25] for these states, a major focus of our effort during the past two years, is presented in the following. Spectroscopic constants for both A' and A" symmetry components of the degenerate 3p 2Π Rydberg state are obtained. The Renner effect is observed for this state and the Renner parameter ε is obtained. This is believed to be the first such measurement for a Rydberg state.

**Experimental**

A laser photolysis/molecular beam/time-of-flight mass spectrometer apparatus, illustrated in Fig. 1, enabled REMPI spectroscopic studies of low-lying vibrational levels of the 3p Rydberg and B valence states of HCO and DCO to be performed under uniquely favorable conditions. A small concentration (≤ 1-2%) of acetaldehyde (CH₃CHO) in helium was expanded as a free jet from the 0.5 mm orifice of a pulsed valve into a stainless steel vacuum chamber. A 308 nm XeCl excimer laser photodissociated acetaldehyde at the jet orifice. The jet was intercepted by a 2 mm diameter skimmer 20 mm downstream of the jet orifice to produce a molecular beam containing rotationally cold, but vibrationally hot, HCO/DCO radicals. Resonance two-photon ionization (R2PI or 1+1 REMPI) was accomplished with an excimer-pumped frequency doubled dye laser that intersected the molecular beam at a
position 50 mm further downstream. HCO\(^+\)/DCO\(^+\) REMPI ions were accelerated along the 1.3 m flight tube of the mass spectrometer to an electron multiplier detector. Amplified ion signals were digitized, averaged and recorded as a function of dye laser wavelength.

**Vibrational Spectra for the 3p States of HCO and DCO**

An overview of the progressions in the bending vibration \(v_2\) for the A' and A" symmetry components of the 3p \(^2\Pi\) state are presented in Fig. 2 for HCO and Fig. 3 for DCO for the 208-222 nm wavelength range. The observation of separate progressions for both symmetry components permits the first quantitative examination of the Renner effect yet reported for a Rydberg state; the determination of the Renner parameter \(\varepsilon\) for HCO and DCO is discussed below. The subband

![Subband diagram](image)

**Figure 2:** R2PI spectrum of HCO. Partial subband progressions \(3p \ ^2\Pi(A') \leftarrow X^2\Pi \ (0,v_2,0) \leftarrow (0,0,0) \ (K',K'')\) for \(0 \leq v_2 \leq 3\), and \(3p \ ^2\Pi(A'') \leftarrow X^2\Pi \ (0,v_2,0) \leftarrow (0,0,0) \ (K',K'')\) for \(0 \leq v_2 \leq 3\) are labeled.
designations \((K',K'')\) are indicated for each of the labeled vibronic bands. These designations reflect the alternations in parity with vibrational quantum number for this \(^2\Pi\) state; even values of \(K'\) are associated with odd values of the bending vibrational quantum number, \(v_2\). The origin positions for the bands of these progressions are plotted as a function of bending quantum number for \(A'\) and \(A''\) components in Figs. 4 and 5, respectively. The expected difference in zero-point energies between HCO and DCO may be estimated at \(116\pm 50\ \text{cm}^{-1}\), based on previous work.[21] The observed value of \(T_{000}(\text{HCO}) - T_{000}(\text{DCO}) = 92\ \text{cm}^{-1}\) meets this expectation and confirms the vibrational quantum number assignment; indeed the
Figure 4: Extrapolation of the HCO and DCO \((0,v_2,0)\leftrightarrow(0,0,0)\) A''\(\leftrightarrow\)A' progressions. The ordinate gives the energies \(T_{000}(\text{HCO})\) and \(T_{000}(\text{DCO})\). The difference between these terms for HCO and DCO at the position of the zero band is 92 cm\(^{-1}\); this is in agreement with the estimate of 116\(\pm\)50 cm\(^{-1}\) based on previous work, and establishes the absolute vibrational quantum numbering for the upper state bending mode.

Figure 5: Extrapolation of the HCO and DCO \((0,v_2,0)\leftrightarrow(0,0,0)\) A''\(\leftrightarrow\)A' progressions. The ordinate gives the energies \(T_{000}(\text{HCO})\) and \(T_{000}(\text{DCO})\). The difference between these terms for HCO and DCO at the position of the zero band is 92 cm\(^{-1}\); this is in agreement with the estimate of 116\(\pm\)50 cm\(^{-1}\) based on previous work, and establishes the absolute vibrational quantum numbering for the upper state bending mode.
curves of Figs. 4 and 5 would intersect for any other choice. The vibrational assignments confirm, moreover, that indeed these spectra belong to an upper state with one quantum of electronic angular momentum. Many additional vibronic bands, unlabeled in Figs. 2 and 3, were observed; band origin positions for these bands are given in Tables I to V (p. 34). Many of these bands originate from vibrationally excited levels of the ground electronic state; this redundancy in the determination of the band origins provides a useful check on our wavelength calibrations. In addition to the spectroscopic constants for the $3p^2 \Sigma^+$ states of HCO and DCO, discussed below, these measurements yield the previously unknown anharmonicity constant $x_{22}$ for the $X^2\Pi$ ground state of DCO and a significantly more precise value of $x_{22}$ for $X^2\Pi$ HCO.

**Rotational Spectra; Symmetry Assignments**

Rotational spectra for the $(0,v_2,0)\leftarrow(0,0,0)$ progressions of the $A''$ symmetry component with $0\leq v_2 \leq 3$ for HCO and $1\leq v_2 \leq 4$ for DCO are displayed in Figs. 6a-6d and Figs. 7a-7d, respectively. These spectra show the simple, open, perpendicular band structure, with P, Q, and R branches, expected for an $A'' \leftarrow A'$ transition. Indeed the positive sign of the combination defects $[R(N)-Q(N+1)]-[Q(N)-P(N+1)]$ determined for the $(0,1,0)\leftarrow(0,0,0)$ and $(0,3,0)\leftarrow(0,0,0)$ bands confirms an upper state of $A''$ symmetry for these one-photon absorptions. The subband assignments follow from the rotational structure of each band; $(K',K'') = (1,0)$ subbands have P branches that originate with P(2), while $(0,1)$ subbands exhibit a P(1) transition.

Figs. 8 and 9 reveal the rotational structures of bands located slightly to the red of the $A''(0,1,0)\leftarrow(0,0,0)$ bands for HCO and DCO, respectively. These bands are
Figure 6: Rotational structure of perpendicular ($\Delta K = \pm 1$) subbands of the HCO $3p \ ^2\Pi (A^\prime) \leftarrow X^2\Pi (A^\prime) (0,v_z,0) \leftarrow (0,0,0)$ progression.
Figure 7: Rotational structure of perpendicular ($\Delta K = \pm 1$) subbands of the DCO $3p^2 \Pi (A^r) \leftarrow X^2 \Pi (A') (0,v_2,0) \leftarrow (0,0,0)$ progression.
parallel $\Sigma' \leftarrow \Sigma'$ vibronic bands with no Q branches. Because parallel bands are forbidden for $\Sigma'' \leftarrow \Sigma'$ transitions, but allowed for $\Sigma' \leftarrow \Sigma'$ transitions, the upper state for these bands is of $\Sigma'$ symmetry in agreement with the symmetry assignments introduced above. These bands are therefore $(K',K'') = (0,0)$ subbands of the $\Sigma' \leftarrow \Sigma'$ $(0,1,0) \leftarrow (0,0,0)$ transitions.

**The Renner effect**

In our previous studies[21] of the two-photon resonant (2+1) REMPI spectra of the $3p \ ^2\Pi$ state, only the $\Sigma''$ symmetry component was observed, even though two-photon absorptions to the $\Sigma'$ component are formally allowed. For this reason we were unable to quantitatively evaluate the magnitude of the Renner-Teller vibronic splitting for this state. Indeed we have found no example in the literature of any other determinations of the Renner parameter $\varepsilon$ for a Rydberg state. The present observations of both $\Sigma'$ and $\Sigma''$ components are therefore of considerable importance.

Hougen and Jesson[26] and Brown and Jorgensen[27] have given expressions
for the vibrational energies of the upper (A\textsuperscript{''}) and lower (A\textsuperscript{'}) components of a \textsuperscript{2}\Pi state of a linear triatomic molecule, split by the Renner-Teller vibronic interaction, valid for small values of the Renner parameter \(\varepsilon\), under conditions where vibronic anharmonicity cannot be neglected. Use of these expressions for the upper state (e.g., Frye and Sears\cite{28}) and the usual vibronic energy expression\cite{29} for the ground state in a nonlinear least squares fitting to the band positions of Tables I to V (p. 34) yields the vibrational spectroscopic constants given in Tables VI and VII (p. 34). The upper state rotational constants given in Table VI were determined by combination difference analyses of rotational line positions. Values determined for the rotational constants of the X\textsuperscript{2}\Pi ground states of HCO and DCO are in good agreement with more accurate values, previously measured with higher resolution spectroscopy.\cite{30}

The measured value of the Renner parameter, \(\varepsilon = 0.07\), for HCO and DCO is smaller than values of (\(\pm\)) \(\approx 0.15\) to 0.55 measured for \textsuperscript{2}\Pi valence states of many triatomic molecules, e.g., HCO, NCS, BO\textsubscript{2}, CO\textsubscript{2}+, NCO, CNC, N\textsubscript{2}O\textsuperscript{+}.\cite{28,31-36}

**REMPI Spectra for the B(A\textsuperscript{'}) \leftrightarrow X(A\textsuperscript{'}) Band System**

Quite recently two groups have observed LIF from the B(A\textsuperscript{'}) valence state of HCO\cite{23,24}, and the use of this transition for LIF measurements of HCO flame density profiles has been demonstrated.\cite{37} The new LIF measurements significantly extend the classic studies of Dixon\cite{38}, who used emission spectroscopy to analyze the "hydrocarbon flame bands" of interest to combustion scientists for many years. LIF measurements of the approximate positions of many high-lying vibrational levels of the ground electronic state have been of much importance in the development and
Refinement of DOE supported ab initio calculations of the ground state HCO potential energy surface.[39,40]

We observe quite strong R2PI (1+1 REMPI) B(A') ← X(A') vibronic bands of HCO and DCO in the 227-258 nm wavelength region. Overviews of these bands are presented in Figs. 10 and 11. The notation used for labeling the upper states of these vibronic bands is that adopted by Dixon[38] and recent authors[23] with modes 1, 2, and 3 designating the CH(CD) stretch, CO stretch, and HCO(DCO) bending vibrations, respectively (the CO stretch and HCO bend are interchanged from the convention followed for linear HCO). The strength and clarity of these bands is somewhat unusual for REMPI spectra of valence band transitions. In contrast to the strong REMPI spectra of Fig. 10, the LIF spectra for HCO become progressively weaker as the excitation energy increases; the (0,0,3)←(0,0,0) band is 12 times weaker than the (0,0,0)←(0,0,0) band in LIF. Moreover, levels above the B(1,1,0) state are not observed via LIF excitation. We obtain the previously unmeasured fundamental vibrational frequencies for the B state of DCO (CD stretch = 1953 cm⁻¹, CO stretch = 1212 cm⁻¹, DCO bend = 922 cm⁻¹). Our values for the fundamental vibrational frequencies for the B state of HCO agree well with the earlier LIF studies.[23,24]

It seems likely that both LIF and REMPI measurements of HCO profiles can be conveniently measured with B←X vibronic bands; it will be of interest to compare diagnostic measurements performed with these transitions to previous results obtained with the 3p Rydberg (0,6,0)←(0,0,0) transition.[3,6]
Figure 10: R2PI vibronic spectra of the B(A') $\leftrightarrow$ X(A') transition of HCO. The $(v_1, v_2, v_3)$ labels are given for the upper states of prominent bands.

Figure 11: R2PI vibronic spectra of the B(A') $\leftrightarrow$ X(A') transition of DCO. The $(v_1, v_2, v_3)$ labels are given for the upper states of prominent bands.
B. REMPI Spectroscopy of the Ethynyl Radical

Spectroscopic observations of the electronic states of the ethynyl radical have eluded investigators since the initial detection of matrix isolated C$_2$H in 1964.[41] Only the $A^2\Pi \rightarrow X^2\Sigma^+$ band system has been successfully analyzed to date.[42-52] We have conducted an extensive search for the spectral signatures of potential (2+1) and (3+1) REMPI transitions via 3s and 3p Rydberg states of C$_2$H, a radical of key importance in the chemistry of hydrocarbon flames.[20] Extensive previous searches for one-photon transitions of C$_2$H in the 125-180 nm region with C$_2$H$_2$, C$_2$HBr, and CF$_3$C$_2$H precursors by conventional flash photolysis vacuum ultraviolet (VUV) absorption spectroscopy have been unsuccessful.[53,54]

Our studies resulted in the observation of a new electronic state of C$_2$H, tentatively assigned, by Koures and Harding,[55] as the 3$p\sigma^2\Pi$ Rydberg state, located about 9 eV above the ground $X^2\Sigma^+$ state.[20] The observed absorptions originate from vibrationally excited C$_2$H and C$_2$D formed in the photodissociation of C$_2$H$_2$, C$_2$D$_2$ and C$_2$HD at 193 nm in a molecular beam. Two-laser experiments and REMPI spectroscopy of photofragments of the dissociation of C$_2$HD were used to assign the carriers of the observed spectra conclusively to C$_2$H and C$_2$D. Two-photon resonant, three-photon ionization (2+1 REMPI) of C$_2$H and C$_2$D is accompanied by substantial fragmentation to C$_2^+$ ions, caused by multiple photon absorption by resonantly excited C$_2$H and C$_2$D. The identity of the lower C$_2$H electronic state(s) ($A^2\Pi$ or $X^2\Sigma^+$) was not established.

The (2+1) REMPI spectra of C$_2$H and C$_2$D have the appearance of complex
superpositions of several poorly resolved subbands. These weak and somewhat diffuse band spectra are in marked contrast with the strong well-defined Rydberg spectra observed with the REMPI method for other small polyatomic radicals,[56] including HCO[21] and CH3[57,58]. This result and the previous unsuccessful attempts to observe the one-photon VUV Rydberg spectrum of C2H[53,54] leaves little doubt that the low-lying Rydberg states of C2H are strongly predissociated. The widths of the narrowest spectral features indicate a predissociation lifetime of about 10^{-11} s. Even though the ethynyl cation is stable, Koures and Harding[55] have suggested that some of the C2H Rydberg states may be directly dissociative along the C-H coordinate.

C. REMPI Spectroscopy of New Electronic States of C2

The electronic states of the C2 radical have been extensively studied because of the importance of C2 in astrophysics and combustion chemistry. *Ab initio* calculations of potential energy curves are available for 62 valence states; of these, 29 are possible bound states for which molecular parameters have been calculated.[59] Spectroscopic constants were known for 14 of these bound states at the inception of our studies. As our work was in progress, Fourier transform emission spectroscopy was used to obtain spectroscopic constants for the previously unobserved B1\Delta_g and B' 1\Sigma_g^+ states.[60]

Despite this relatively mature state of knowledge of the electronic states of C2, multiphoton selection rules and the high sensitivity of REMPI spectroscopy made possible our observations of transitions to electronic states inaccessible with older
methods. In our studies \( C_2 \) radicals in the \( A^1\Pi_u \) state were formed in a molecular beam \textit{via} the two-step photolysis of \( C_2H_2 \) at 193 nm:[61]

\[
\begin{align*}
C_2H_2 + hv(193 \text{ nm}) & \rightarrow C_2H + H \\
C_2H + hv(193 \text{ nm}) & \rightarrow C_2(A^1\Pi_u) + H
\end{align*}
\]

The radiative lifetime of the \( C_2(A^1\Pi_u) \) state is long enough \((10^{-5} \text{ s})\) that REMPI ionization from the \( A^1\Pi_u \) state, \textit{via} two-photon resonant excitation of the \( 1^1\Delta_u \) state, was produced with a tunable dye laser timed to fire about 2 \( \mu \)s after the photolysis laser pulse. REMPI ions produced with the tunable dye laser were mass-analyzed with a time-of-flight mass spectrometer (TOFMS) (see Fig. 1).

**Observed Spectra**

Thirteen vibronic bands assigned to the \( 1^1\Delta_u \leftarrow A^1\Pi_u \) transition of \( C_2 \) were observed with \((2+2)\) REMPI spectroscopy for laser wavelengths from 370 to 480 nm. The measured term value \( T_e = 57720 \pm 20 \text{ cm}^{-1} \) for the previously unobserved \( 1^1\Delta_u \) state is in good agreement with upper limits given by \textit{ab initio} calculations. An approximate (Morse) potential energy curve for this new \( 1^1\Delta_u \) electronic state is illustrated in Fig. 12; its spectroscopic constants are given in Table VIII (p. 19).

The discovery of the \( B^1\Delta_g \) state, reported[60] shortly after our observation of the \( 1^1\Delta_u \) state,[62] led us to a successful search for the previously

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{morse_potential_energy_curves}
\caption{Morse potential energy curves for experimentally observed singlet states of \( C_2 \). The recently discovered \( B^1\Delta_g \) and \( B' \) \( ^1\Sigma_g^+ \) states are not shown.}
\end{figure}
Table VIII: Spectroscopic Constants for the 1^1Δ_u State of C_2

\[
\begin{array}{ll}
D_o = 12,990 \text{ cm}^{-1} & B_e = 1.361 \pm 0.002 \text{ cm}^{-1} \\
T_e = 57.720 \pm 2 \text{ cm}^{-1} & \alpha_e = 0.026 \pm 0.002 \text{ cm}^{-1} \\
\omega_e = 1150 \pm 1 \text{ cm}^{-1} & D_e = 7.7 \times 10^{-6} \text{ cm}^{-1} \\
\omega_e \chi_e = 21.3 \pm .5 \text{ cm}^{-1} & r_e = 1.437 \pm 0.002 \AA \\
\nu_{\infty} = 49097 \pm 1 \text{ cm}^{-1} (1^1Δ_u \leftarrow \Pi_u^1) \\
\end{array}
\]

\*a\) Calculated using \( D_o = 6.21 \text{ eV} \).

unknown 1^1Δ_u \leftarrow B^1Δ_g transition.[63] Six vibronic bands, \((ν',ν'') = (0,0), (0,1), (1,1), (1,2), (2,1) \) and \((2,2)\), for this transition were observed at the precise energies predicted with the spectroscopic constants determined for the 1^1Δ_u and B^1Δ_g states.[60,63,64]

**D. A Flame Sampling Laser Ionization Mass Spectrometer**

We are now operating a unique flame sampling laser ionization mass spectrometer, partially constructed with funds from this grant, designed to efficiently record the REMPI spectra of radical intermediates of importance in the combustion of hydrocarbon fuels and the incineration of chlorinated organic molecules.

There are two quite different approaches that may be followed in performing REMPI spectroscopy of radical combustion intermediates. The first method is to search for the REMPI spectra of a given radical, of known importance in combustion, with the use of a photolytic precursor for radical generation. Until now this is the approach that we have followed in our studies of HCO, C_2 and C_2H, discussed above. Our experience has demonstrated both the advantages and shortcomings of this procedure. The REMPI spectroscopic studies of H, O, HCO, and CH_3 provide
excellent examples of radicals of key importance in hydrocarbon combustion that, thanks to this approach, can be routinely monitored for unique evaluations of chemical kinetic models. On the negative side, many radicals, e.g., C₂H, may have strongly predissociated electronic states that yield weak and diffuse REMPI spectra, unsuitable for diagnostic measurements. Although it may be argued that new knowledge of the electronic states of radical species, whether predissociated or not, is certainly valuable, it would be advantageous to efficiently screen those radicals of interest that happen to possess suitable REMPI spectral signatures from those that do not. The apparatus described below will provide this screening for radical intermediates in the combustion of chlorinated organics proposed for study here.

A schematic diagram of our flame sampling laser ionization mass spectrometer is given in Fig 13. The flame sampling and TOFMS components are of conventional design, well documented in previous mass spectrometric sampling studies of the species profiles of hydrocarbon flames.[65] The novel aspect of this apparatus is the use of REMPI as an ionization source. In one mode of operation (mode 1) neutral radicals are sampled from a low pressure (30 Torr) premixed laminar flame source with a water cooled, rhodium coated, copper skimmer of 0.2 mm diameter orifice. A second skimmer of 2 mm diameter intercepts the expanded jet at a position 12 mm downstream of the first and forms a well-collimated molecular beam. The beam passes between the acceleration plates of the TOFMS where REMPI ionization of radical species is accomplished with a pulsed tunable dye laser. A second mode of operation (mode 2) is feasible in which REMPI ions are directly produced within the
flame zone. These ions are sampled by the first skimmer, accelerated, focused and then decelerated by ion optics to place them between the acceleration plates of the mass spectrometer. Upon the arrival of the ions, the acceleration plates are pulse-gated to deflect the ions upward along the axis of the TOFMS. This second method, while considerably more difficult to implement, has the advantage that in situ REMPI provides an ionization signal with the spectral signature of a given radical that might otherwise be lost because of alterations associated with the sampling process itself. A knowledge of the mass of the parent ion, and of the masses of possible daughter ions produced by fragmentation or ion-molecule reactions, permits identification of the flame radical resonantly ionized by the laser. During the coming year, this second mode of operation will be tested by the detection of HCO from a methane/oxygen flame, but this will be given a lower priority than the (mode 1) REMPI studies of radical intermediates of the combustion of chlorinated organics discussed in Section IV below.

Figure 13: Schematic diagram of flame sampling laser ionization mass spectrometer. REMPI spectroscopy of radical intermediates in CHC combustion will be performed with the laser focused between the acceleration plates (mode 1).
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