MULTIPHOTON IONIZATION DETECTION OF CH, CARBON ATOMS, AND O₂ IN PREMIXED HYDROCARBON FLAMES

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Measurements of the multiphoton ionization (MPI) spectra of CH, C atoms, and O₂ have been made in atmospheric-pressure CH₄/air and C₂H₆/air flames in the 280-315 nm region. The transitions involved are D ²Π₁ → X ²Π₀ and E ²Σ⁺ → X ²Π₀ for CH, the 2D₂ → 2P₂ and 1S₀ → 1D₂ multiplets for carbon atoms, and (3σ) ²Π₂ → X ³Σ⁻ for O₂. Unusual rotational line intensities are observed in the CH spectra, which double resonance experiments show arise from near resonance with the intermediate C ²Σ⁺ state. The MPI spectrum of O₂ is much more intense in flames compared to room-temperature, atmospheric-pressure conditions.

1. Introduction

Resonance-enhanced multiphoton ionization (MPI) has been used to detect a variety of free radicals and stable species in flames, including H [1-3], O [3,4], C [5], CO [6], NO [7,8], PO [9], C₂O [6], CH₃ [5,10], and trans-1,3-butadiene [11,12]. The high sensitivity of the method makes it attractive for diagnostic applications in flames and plasmas, especially for atoms and molecules which do not fluoresce strongly. However, a limitation to wider use of MPI is the paucity of information concerning the high-lying states of flame species. Recent experiments of photolytically produced radicals such as CH [13-16] and HCO [18,19] provide MPI spectra of high-lying Rydberg and valence states to guide the flame experiments.

In the present study CH radicals, carbon atoms, and molecular oxygen are detected within atmospheric-pressure CH₄/air and C₂H₆/air flames. The spectra are all due to two-photon resonant, three-photon ionization (“2+1” MPI) and have been observed and assigned previously in molecular beam and room temperature cell studies. While the carbon atom lines and O₂ bands reported here are similar in appearance to previous spectra, the CH band is strikingly different in that several branches are missing and only a few rotational lines appear. Evidence is presented that this unusual rotational line intensity in the CH spectrum arises from near resonance with an intermediate electronic state. The implications of the present measurements for detecting CH and O₂ in flames will also be discussed.

2. Experimental approach

A Nd:YAG-pumped, frequency-doubled dye laser produced 10 ns, 1-2 mJ pulses in the 280-315 nm range (see fig. 1). The light was passed through an adjustable aperture, focused using a 500 mm focal length lens, and then directed along the centerline of a 5.3 cm long analytical slot burner. Typically a 1-2 mm aperture was used to reduce the beam energy to 300-400 μJ/pulse. Atmospheric-pressure mixtures of CH₄/air and C₂H₆/air were burned at various equivalence ratios, and ionization signals were collected with a single, 1 mm diameter tungsten rod held at +1000-1500 V relative to the grounded burner body. The transient current induced in this electrode was detected with a charge-sensitive amplifier and monitored with a boxcar integrator. The multiphoton...
ionization spectra of CH, carbon atoms, and O₂ were found to be identical in both flames.

Double-resonance experiments were also carried out on CH. For these measurements 20% of the second-harmonic of the Nd:YAG laser at 532 nm was split off to pump a second dye laser, and the dye laser output was then frequency doubled to produce approximately 200 μJ/pulse at 312 nm. This second laser was used to selectively pump a particular rotational line in the C₂Σ⁺→X²Π₁ band, while scanning the first dye laser and monitoring the MPI spectra due to both the D++X and DτCtX transitions. The two laser beams were directed antiparallel and focused with 300 mm focal length lenses to overlap spatially and temporally in the reaction zone of the methane/air flame.

### 3. Results and discussion

#### 3.1. CH

The multiphoton ionization spectrum of the CH radical was detected in the high-temperature primary reaction zones of the CH₄/air and C₂H₆/air flames. MPI spectra of CH have been observed previously in multiphoton photodissociation/ionization studies of ketene, t-butyl nitrite, and bromoform [13–16]. Assignment of the band near 312 nm to 2+1 ionization involving the D²Π₁(ν' = 2) ← X²Π₁(ν'' = 0) transition was made by analysis of the photoelectron spectrum [14]. Fig. 2 (top) shows the flame results near 312 nm. The observed spectrum is strongest in the reaction zone and falls off quickly at higher flame positions. The best signal-to-noise ratio appears for low laser energies (100 μJ/pulse), since at higher laser intensities a non-resonant background ionization signal was found to increase faster than that due to CH ionization.

The photodissociation/ionization spectra of Chen et al. [13–15] show smooth rotational envelopes in all of the branches, and provide the assignment shown in fig. 2. In contrast, the flame spectra are strongly peaked at Q(8) near 311.9 nm, the R branch is barely visible, and the O, P, and S branches are missing entirely. (For notational simplicity, Q(N) refers to the spin doublets Q₁(N) and Q₂(N); the large A doubling of CH was not observed in the present measurements – see below.) Assuming thermal equilibrium, one would expect the rotational populations to peak between N'' = 6 and 7 for flame temperatures between 1700 and 2000 K.

Fig. 2 (bottom) shows the excitation spectrum of CH C²Σ⁺(ν' = 0) ← X²Π₁(ν'' = 0) fluorescence, which was recorded simultaneously with the ionization signal using a monochromator to view the C→X emission at 314.5 nm. The smooth rotational envelope of this excitation scan resembles closely the published emission spectrum for CH [20]. This shows that the unusual rotational distribution observed in the ionization spectrum (fig. 2, top) does not result from non-equilibrium ground state rotational level populations in the CH₄/air flame. Note that the C→X fluorescence excitation spectrum overlaps the 2+1 ionization spectrum at the one-photon level. Since the rotational numbering of the R branch of the C→X band increases to the blue, while the D→X Q branch is red degraded, the one-photon energy difference between the MPI and fluorescence spectra for a given rotational number exhibits a minimum. This occurs at the N'' = 8 rotational level near 311.9 nm, and thus it is likely that the highly peaked rotational distribution of the MPI Q branch results from the near resonance with the R branch of the C²Σ⁺ intermediate state. Supporting this interpretation is the absence of observ-
The multiphoton ionization spectrum of CH (top) arises from two-photon excitation followed by absorption of a third photon of the same energy to reach the ionization continuum. Line positions for the P, Q, and R branches are based on the study of Chen et al. [15]; the turning point for the R branch occurs for $N'' = 7$. The MPI spectrum is compared to the one-photon laser-induced fluorescence excitation scan in the same wavelength region (bottom). The weak lines in this spectrum are due to OH fluorescence.

Fig. 2. The multiphoton ionization spectrum of CH (top) arises from two-photon excitation followed by absorption of a third photon of the same energy to reach the ionization continuum. Line positions for the P, Q, and R branches are based on the study of Chen et al. [15]; the turning point for the R branch occurs for $N'' = 7$. The MPI spectrum is compared to the one-photon laser-induced fluorescence excitation scan in the same wavelength region (bottom). The weak lines in this spectrum are due to OH fluorescence.

able $A$ doubling, which is consistent with the parity selectivity caused by resonant enhancement from a $\Sigma$ electronic state [21].

The D state of CH arises from the doubly excited $2p\pi^2$ configuration and thus can be optically excited from the $2p\sigma^22p\pi$ ground state via the $2p\sigma2p\pi^2$ $C$ state [22]. If one considers the $D \leftrightarrow X$ Q(8) transition in terms of possible stepwise excitation processes, then only R-branch transitions of the C state occur at energies which are nearly resonant at the one-photon level. For the $D \leftrightarrow X$ transition the stepwise excitation path which is most favorable involves the R(8) transition of C$\leftrightarrow X$ followed by P'(9) of the D$\leftrightarrow C$ band. Along this path the energy of the first photon is detuned by only 5–7 cm$^{-1}$ from that required to excite the two-photon D $\leftrightarrow X$ Q(8) transition. The next strongest two-photon D $\leftrightarrow X$ line, Q(9), is farther detuned (35 cm$^{-1}$) from its closest intermediate level ($N'' = 10$ of the C state), and its intensity is 4–5 times weaker in the two-photon MPI spectrum. The Q(7) line is detuned by 46 cm$^{-1}$ and is even weaker. All the other Q-branch transitions are at least 75 cm$^{-1}$ detuned from a C state R-branch rotational level and are barely discernible in fig. 2. It is likely that a similar enhancement for the fragmentary R branch of the D $\leftrightarrow X$ band near 310.7 nm also occurs. A single doublet is observed and is probably the enhanced R(12) line which gains intensity from the C$\leftrightarrow X$ R(12) transition, detuned by approximately 10 cm$^{-1}$.

A fragmentary branch of CH was also observed near 290 nm and consists of the S(1–5) doublets of the transition assigned to $E'$ $2\Sigma^+ \leftrightarrow X^2\Pi$, by Chen et al. [15]. However, none of the other branches reported by Chen et al. in this wavelength region was detected, and therefore the MPI flame signal again appears to be enhanced by near resonance with the intermediate $C^2\Sigma^+$ state of CH, this time involving the $\nu' = 1$ level [23, 24]. Here the enhancement is less selective, since the C($\nu' = 1$) $\leftrightarrow X(\nu'' = 0)$ R branch proceeds in the same direction as the S branch of the $E'$ $\leftrightarrow X$ band, so that a broader range of rotational lines is enhanced in the 2+1 MPI spectrum.

Two additional experiments were conducted to confirm the assignment of the multiphoton ionization spectrum shown in fig. 2 to CH. First, the Q(9) D $\leftrightarrow X$ line was pumped while a second laser of lower intensity was scanned across the R(9) C$\leftrightarrow X$ line. A 40% decline in the ionization signal was recorded when the frequency of the second laser was resonant with the R(9) line, showing that near-saturation of the one-photon C$\leftrightarrow X$ transition significantly depletes the ground state rotational level being pumped and thereby reduces the CH ionization signal. In a second experiment the D state was probed using a double-resonance method with the pump dye laser providing rotational specificity in the excitation of the intermediate C state. The ionization sig-
nal then resulted from stepwise excitation \( X \rightarrow C \rightarrow D \rightarrow \) ionization. The ionization step is non-resonant and can be excited by either laser frequency. For example, the pump laser was fixed at \( R(8) \) of \( C \rightarrow X \), thus populating the \( N' = 9 \) rotational level of the \( C \) state. Scanning of the probe laser gave three new doublets in the ionization spectrum, \( P'(9), Q'(9) \) and \( R'(9) \), which had not been observed previously. These additional resonances disappeared when either the pump or probe laser was blocked. Adding the photon energy of the \( R(8) \) pump laser to the one-photon energies of these new resonances gives total energies which correspond to the published positions of the \( D \rightarrow X \) \( Q(8), R(8), \) and \( S(8) \) lines, respectively [15]. While the single-laser \( Q(8) \) MPI signal is enhanced by the accidental near-resonance at \( N' = 9 \) of the \( C \) state, the two-laser method is resonant at both laser frequencies and gives a signal which is at least 5 times stronger.

In contrast to our CH multiphoton ionization spectrum shown in fig. 2, Chen et al. [15] observed smooth rotational envelopes and complete \( O, P, Q, R, \) and \( S \) branches upon excitation of the \( D^2 \Pi \) state in the same spectral region. Recently, Hudgens et al. [16] have published a spectrum similar to that reported by Chen et al. In these prior investigations the laser intensities were considerably higher than in the present study, and in both cases a precursor molecule was photolyzed before detecting the CH fragment via MPI during the same laser pulse. It is likely that the resonant enhancement due to the \( C^2 \Sigma^+ \) state occurs over a wider spectral range, but whether or not power broadening of the intermediate state is sufficient to account for their observed spectra is uncertain. Neither study observed the \( D \rightarrow X \) \( (0, 0), (1, 0), \) or \( (3, 1) \) bands, nor the \( E' \rightarrow X \) \( (1, 0) \) band.

The estimated positions of these transitions place the energy of the first photon at least half of a vibrational quantum away from being in resonance with the \( C \) state, and thus the expected resonance enhancement is minimal. In our flame experiments increasing the laser intensity results in a greater number of Q-branch transitions being observable (typically four or five doublets), but the overall signal-to-noise ratio degrades due to increased background ionization.

CH has been extensively studied in flames by using laser-induced fluorescence detection of the strong \( A^2 \Delta \rightarrow X^2 \Pi \) band [25–34]. For monitoring low CH concentrations this approach is the most sensitive. However, the multiphoton ionization transitions detected in the present work exhibit signal-to-noise levels comparable to laser-induced fluorescence on the \( C^2 \Sigma^+ \rightarrow X^2 \Pi \) transition (fig. 2) [35]. In addition, two-color stepwise ionization may be useful in providing pin-point spatial resolution using crossed laser beams.

3.2. Carbon atoms

During the course of the measurements on CH, ionizing transitions due to seven atomic carbon lines from the \( ^1D_2 \leftarrow ^3P_2 \) multiplet were also observed at 286.76, 286.83, 286.88, 286.91, 287.00, 287.02, and 287.12 nm, along with the \( ^1S_0 \leftarrow ^1D_2 \) line at 313.48 nm [36,37]. While these carbon lines appeared most strongly in the primary reaction zones of the \( CH/air \) and \( C_2H_2/air \) flames, their spatial overlap with the \( O_2 \) spectrum (fig. 3) was sufficient to provide a simultaneous, convenient wavelength calibration. For calibration purposes numerous two-photon resonances of the carbon atom can be excited in the 279–341 nm spectral region [36]. Free carbon atoms are not likely to be indigenous to these flames.

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\text{Fig. 3. The multiphoton ionization of carbon atoms appears as the seven intense lines at } \approx 286.9 \text{ nm. For this spectrum the laser beam irradiated the flame in the primary reaction zone. The congested underlying spectrum arises from the multiphoton ionization of } O_2 \text{ (see also fig. 4).}
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but are probably produced by photolysis of hydrocarbons during the laser pulse. Efficient neutral carbon production has been shown to occur in the ultraviolet laser irradiation of a variety of hydrocarbons [36,38,39]. In the present study the strongest spectrum due to carbon atom ionization is observed upon irradiation of the hottest flame regions, suggesting that one or more radicals are being photolyzed. In fact, the C$^2\Sigma^+$ state of CH, which correlates to ground state C($^3P$) + H atoms, is weakly predisassociative in this spectral region [22] and thus is a possible precursor for carbon atom production.

3.3. O$_2$

The rich pool of free radicals and stable molecules within flames creates ample opportunities for molecular and atomic interference of unknown origin. An example is found in the recent work of Meier and Kohse-Höinghaus in their measurement of CH$_3$ radicals in low-pressure CH$_4$/O$_2$ flames [10]. While 2+1 MPI detection at 286 nm (4p$^2$A'$_2$ ← $X^2A^+_2$) yielded stronger signals than at 333 nm (3p$^2$A'$_2$ ← $X^2A^+_2$) in a flow-reactor apparatus, the methyl radical signal at 286 nm was overwhelmed in their flame measurements by an intense molecular background. They describe the unknown interference as “a considerable number of almost evenly spaced lines... between 284 and 288 nm which were strongest in intensity close to the burner surface”. The spectrum appeared throughout rich CH$_4$/O$_2$ and C$_2$H$_4$/O$_2$ flames as well as in lean H$_2$/O$_2$ flames.

The present study identifies O$_2$ as the carrier of this background interference spectrum. Fig. 4 shows the spectrum of O$_2$ taken in the preheat region, upstream from the reaction zone of a methane/air flame; here the strongest signals were observed. With the flame extinguished, the signal was found to be 20-40 times weaker but was still observable in room air. The spectrum disappeared in a room temperature cell containing N$_2$ but was present in pure O$_2$ and in mixtures of O$_2$/N$_2$ and O$_2$/Ar. High-temperature room air ($T$=600 K) produced with a heat gun gave signals of comparable magnitude to those found in the flame. Downstream from the reaction zone of lean ethylene/air flames the characteristic one-photon resonant, two-photon ionization (1+1) spectrum of NO appeared weakly at wavelengths shorter than 285 nm [7].

The 284-288 nm spectrum shown in fig. 4 arises from a 2+1 ionization process which involves the (3σ$^r$) $^3\Pi_g(v'=2)$ ← $X^3\Sigma^+_g$ ($v''=0$) transition of O$_2$. The first observations and assignment of this band were made by Sur et al. and Katsuma et al. using pulsed supersonic molecular beams [40,41]. A more extensive room-temperature spectrum from 276 to 306 nm has recently been published by Johnson et al. [42]. The flame spectrum presented here was taken with lower laser intensity than used in the previous studies of the O$_2$ spectrum, and reveals a rotationally resolved band with a limiting width for the narrowest lines of 2 cm$^{-1}$. This width is three times less than that observed by Sur et al. [40], in part due to a narrower laser bandwidth (0.4 cm$^{-1}$ in the present study versus 1.5 cm$^{-1}$), but mostly because the lower intensity reduced the power broadening of the transitions.

Additional bands due to the multiphoton ionization of O$_2$ were observed in both flames and in room air near 304 and 301 nm and are assigned to two-photon excitation of the (3σ$^r$) $^3\Pi_g$($v'=0$) and (3σ$^r$) $^1\Pi_g$($v'=0$) states, respectively [40,43]. No transitions from vibrationally excited ground state levels or electronically excited states of O$_2$ were detected in either flame.
O₂ is a major flame constituent under many conditions, with the result that its multiphoton ionization spectrum can be intense. However, for quantitative detection of O₂ in flames, the (3σg) 3Πg ← X 3Σg⁻ transition has somewhat limited utility due to the quenching behavior of the intermediate 3σ Rydberg state. O₂/N₂ and O₂/Ar mixtures at atmospheric pressure give significantly larger absolute signals than does pure O₂, indicating that ground state O₂ efficiently quenches the 3σ excited electronic state. This sensitivity to the local flame composition will hinder even relative concentration measurements in any combustion environment. In addition, the observed MPI signal was found to depend upon the temperature and thus on the density. Upon heating room air from 295 to 600 K the integrated band intensity increased by 20–40 times, whereas the density decreased by only a factor of two. In these measurements the applied electric field was far below the gas avalanche regime, so that the ion collection efficiency varied little with gas density. It is clear that the final step involving absorption from the 3σ Rydberg state to the ionization continuum is not optically saturated under our experimental conditions, and therefore the MPI signal intensity depends upon the effective lifetime of this intermediate electronic state. The sensitivity to quenching will be much reduced for flame studies at subatmospheric pressure and can be diminished by using shorter laser pulses and higher pulse energies. With an effort comparable to that expended on NO [44], quantitative flame measurements of O₂ using multiphoton ionization detection should be achievable.

4. Conclusions

Two-photon resonant, three-photon ionization spectra have been detected for CH, carbon atoms, and O₂ in premixed hydrocarbon flames in the 280–315 nm wavelength region. Unusual rotational line intensities arise in the CH spectra due to near resonance with the C 2Σ⁺ state at the one-photon level. The O₂ MPI signal intensity is found to vary dramatically with temperature and composition, indicating the 3σ Rydberg state can be efficiently quenched. Photolysis of hydrocarbon flame species is the likely cause of the observed carbon atom transitions, which provide a convenient wavelength calibration in the ultraviolet region.

References