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Atmospheric Pressure Acetylene Detection by UV Photo-fragmentation and Induced C₂ Emission

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Detection of C₂H₂ via UV photo-fragmentation, followed by monitoring the C₂H₂ fluorescence, is explored at atmospheric pressure and at temperatures of 295 K, 600 K, and 800 K, for excitation wavelengths 210 to 240 nm using a broadband laser source (∼3 cm⁻¹ fwhm). At the lower temperature, C₂ emissions correlate closely with C₂H₂ and X absorption bands, and the excitation spectra suggest a higher transition probability for the ν₄ = 2 and 3 states than for the ν₄ = 0 and 1 states. As temperature increases, the excitation spectra exhibit a higher nonresonant background.

INTRODUCTION

Acetylene (C₂H₂) is an important intermediate species in hydrocarbon combustion and a key species for soot formation and growth. Moreover, together with CH₄ and C₂H₄, it is one of the dominant hydrocarbon (HC) species found in the partial oxidation products of moderately rich mixtures. Figure 1 shows the makeup of the unburned hydrocarbons (UHC) predicted for the combustion of a homogeneous mixture of n-C₆H₁₆ in an environment typical of a reciprocating engine. All other HC species are present in quantities of less than 1 ppm. Clearly, a method of detecting C₂H₂ would be useful for detecting in-cylinder sources of UHC emissions associated with overly rich mixtures in engines, as well as for evaluating the effectiveness of the mixing processes in a variety of other practical combustion devices. Moreover, if such a detection technique were to be made quantitative, it would be very useful for the validation of chemical kinetic models of hydrocarbon combustion and for developing and validating models for soot formation.

Several techniques have been developed for C₂H₂ detection in flames, e.g., mass spectroscopy of sampled gases (MS), coherent anti-Stokes Raman scattering (CARS), mid-infrared polarization spectroscopy (mid-IRPS), and tunable diode laser absorption spectroscopy (TDLAS). The MS technique suffers from intrusiveness, the CARS and IRPS methods are complex and can suffer from inadequate spatial resolution, and the TDLAS technique provides only line-of-sight information. In contrast, UV photo-fragmentation offers the potential for spatially resolved, planar detection of C₂H₂ using a single laser and inexpensive signal detection optics and cameras. Raiche et al. have shown that C₂H₂ can be detected in low-pressure flames by monitoring C₂ fluorescence with the excitation laser tuned to a known C₂H₂ absorption line. However, nonresonant wavelengths also produced C₂ emissions, indicating potential interference from other species. Recently, Osborne and Frank have explored the possibility that Swan band fluorescence of C₂ observed in CO-imaging studies of methane/air flames is associated with the photo-fragmentation of C₂H₂ to produce excited C₂. Similar fluorescent interference has been observed in CO measurements in engines. Osborne and Frank evaluated seven prospective C₂ precursor molecules, including C₂H₆, CH₄, and C₂H₄—the three hydrocarbon species dominating the partial-oxidation products shown in Fig. 1. Of these three species, only C₂H₂ produced significant Swan band emissions. Consequently, the likelihood of significant interference from other hydrocarbon species in the products of moderately rich combustion is small. Like the work of Raiche et al., the Osborne and Frank experiments were performed at low pressure (5 Torr). The experiments described in the present work are aimed at determining whether laser-induced photo-fragmentation can potentially serve as a viable diagnostic for high-pressure detection of C₂H₂-—appropriate to the pressures and temperatures characteristic of practical combustion devices, such as reciprocating engines or gas turbine combustors.

BACKGROUND

In its ground state, C₂H₂ is a linear molecule characterized by five distinct normal vibrational modes: ν₁, symmetric C–H stretch; ν₂, symmetric C–C stretch; ν₃, asymmetric C–H stretch; ν₄, trans-bending; and ν₅, cis-bending. The two bending modes are doubly degenerate and have associated angular momentum quantum numbers l₄ and l₅. In the A state,
C$_2$H$_2$ has a trans-bent, planar structure and, thus, has one fewer vibrational modes. In this case, the modes are numbered differently, with $v_3$ corresponding to the trans-bending mode. Because of the similarity in nuclear positions between the X-state trans-bending mode shown in Fig. 2 and the trans-bent $\tilde{A}$ state, one can expect, on Franck-Condon grounds, that $\tilde{A}$–X transitions will be dominated by $v_3$–$v_4$ vibrational transitions. This expectation is borne out by measured UV absorption spectra.$^5,9$

Rapid rise times in the intensity of C$_2$ Swan $^3\Pi_u$–$^3\Pi_u$ emissions observed in low pressure C$_2$H$_2$ photo-fragmentation experiments$^5,10$ imply that the C$_2$ fragments are unimolecular dissociation products formed during the laser pulse. These fragments are believed to form via a three-photon process,$^5,6,10$ commencing with an initial absorption to the X state, followed by a second absorption and rapid dissociation to create highly excited C$_2$H + H. Absorption of a third photon then yields C$_2$ ($^3\Pi_u$) + H + H. Based on energy considerations, it is not possible to form C$_2$ ($^3\Pi_u$) from C$_2$H$_2$ (X) with only two photons for excitation wavelengths longer than $\sim$185 nm. However, multiple three-photon paths to the final product species, with differing photometric efficiencies, may exist. For example, considering that the dissociation energy $D_0$ of C$_2$H$_2$ (X), yielding C$_2$H (X) + H, is $\sim$46 070 cm$^{-1}$,$^5,13$ we anticipate that C$_2$H (X) can be formed by a single absorption, with excitation wavelengths shorter than $\sim$217 nm. Indeed, C$_2$H$_2$ A–X emission intensity has been observed to drop dramatically for excitation wavelengths below $\sim$216 nm,$^12$ even though the absorption continues to increase with decreasing wavelength. Subsequent, two-photon processes taking C$_2$H (X) to C$_2$ ($^3\Pi_u$) + H might lead to overall process efficiencies that differ significantly from processes requiring an initial two-photon absorption. Accordingly, one objective of this work was to explore the effect of excitation wavelength on the C$_2$ fluorescence intensity.

In a similar vein, we anticipate that vibrationally excited C$_2$H$_2$ may have advantageous Franck–Condon overlap factors with the $\tilde{A}$ state, and hence, could exhibit differing photometric efficiency in the formation of C$_2$ ($^3\Pi_u$). This possibility is supported by vibrationally mediated photodissociation studies,$^{13}$ which have shown that vibrationally excited C$_2$H$_2$ (X) preferentially yields C$_2$H ($\tilde{A}$), whereas direct single-photon excitation of the ground state C$_2$H$_2$ yields products dominated by C$_2$H (X), even though the total excitation energies differ by only 1220 cm$^{-1}$. Moreover, with sufficient vibrational excitation ($v_3 + v'_3 \geq 4$, say), it is energetically feasible to form C$_2$ ($^3\Pi_u$) with only two photons at laser wavelengths accessible with inexpensive, commercial optical parametric oscillators (OPOs). In this work, we, consequently, also examine the effect of temper-
conditions, with the laser tuned to a C2H2 absorption band, the blue-green Swan band emissions were readily visible to the naked eye.

The measured spectrum of C2 d3Πg−a1Πu (Swan) emissions is shown in Fig. 4. The center wavelength of the spectrograph was set to 498 nm, such that Swan emissions from the Δv = 0 and Δv = ±1 bands were visible. Average signal levels were determined by integrating the signal over the Δv = 0 band from 19 240–19 680 cm⁻¹ (519.8–508.0 nm; see Fig. 4) and subtracting a background level determined by integrating over the adjacent, equal pixel-width region, where no signal was observed (18 810–19 240 cm⁻¹, or 531.6–519.8 nm). Figure 4 shows that only C2 Swan band emissions were detected in this spectral region.

Low-resolution excitation scans were performed at a fixed wavenumber increment of 100 cm⁻¹ (50 cm⁻¹ near known strong C2H2 absorption bands) and were followed by more-moderate resolution (20 cm⁻¹) scans to clarify the structure of absorbing regions identified in the low-resolution scans. The OPO line width, before doubling, is specified to be 3–6 cm⁻¹ fwhm. The specification was verified with a Yokogawa model AQ6375 optical spectrum analyzer. The accuracy of the OPO wavelength setting was verified to be better than 2 cm⁻¹ by comparing with emission lines from a mercury calibration lamp. The laser irradiance dependency of several peaks in the excitation spectrum was also examined by varying the laser energy.

The excitation scans were performed at temperatures of 295 K, 600 K, and 800 K in the jet exiting the tube heater. The jet fluid was delivered from a gas cylinder prepared by Matheson Tri-Gas Inc. to have 2% C2H2 in N2. No additional purification or conditioning of the cylinder gas was performed. Jet exit temperatures were measured with a 0.08 mm wire diameter, type R thermocouple, and were maintained within ±10 K of the set point.

RESULTS

A low-resolution fluorescence excitation scan obtained within the jet at ambient pressure and temperature is shown in Fig. 5. Although the C2 emissions are greatest when the photon energy is greater than the C2H–H bond energy D0, the emissions rise steadily as the laser wavelength decreases, and there is no obvious discontinuity that occurs at D0. Rising signal levels could be associated with increased efficiency in either absorption or dissociation processes at higher energies; similar behavior14 observed between 47 000 and 50 600 cm⁻¹ in studies of C2H2 dissociation as detected by H atom REMPI (resonance-enhanced multiphoton ionization) has been attributed to more efficient dissociation.

A moderate-resolution scan of wavelengths with photon energies greater than D0 was also performed to highlight the structure in this region and to search for any emissions peaks that might have been missed with the 50–100 cm⁻¹ scan resolution in Fig. 5. The results are shown in Fig. 6a, which also shows the locations of strong C2H2 absorption band origins.8,9 Likewise, band origins for photon energies less than D0 are shown in Fig. 6b, which reproduces the spectrum of Fig. 5, employing a log scale to better identify bands with low C2 emission intensities. The band origins are labeled following the notation in Watson et al.,8 and Van Craen et al.,9 wherein the symbol V^m denotes the transition mv3−nv4, and the symbol K^l denotes the transition iK^l−j(K^l+1), with K^l being the axial angular momentum quantum number in the Å state.

The spectra shown in Fig. 6 indicate that the C2 Swan emissions were closely correlated with the C2H2 Å ← X absorption probabilities, indicating that more-efficient dissociation with increasing photon energy likely plays a minor role in enhancing the signal levels. Peaks in emission intensity were well represented by the V^m band origins, and the magnitude of the peaks is generally highest for ΔK = ±1, as is the absorption probability. A few peaks, notably the one near 46 800 cm⁻¹ in Fig. 6a and the one near 44 000 cm⁻¹ in Fig. 6b, do not correspond to strong C2H2 absorption lines. However, those peaks are relatively minor and appear to be of little diagnostic utility.

Although the energy considerations discussed earlier indicate that the production of C2 (d3Πg) from ground state C2H2 will require three photons, it is nevertheless of interest to examine the laser irradiance dependency of the more promising...
transitions. Experiments varying the laser irradiance were conducted at each of the six most prominent peaks in the spectrum of Fig. 5, as well as at 230.1 nm, corresponding to the excitation wavelength for CO B $\leftarrow$ X (0,0) transitions. Before conducting each laser irradiance sweep, the laser frequency was set to provide the local peak signal intensity by conducting a search with a resolution of 10 cm$^{-1}$. The results are shown in Fig. 7.

In general, the laser irradiance exponents lie between 2.1 and 3.1. A measure of the uncertainty in the exponent, $\pm 0.3$, was obtained by finding the change in the exponent required to reduce the power-law fit correlation coefficient from an average value of 0.995 to 0.990. Within that uncertainty, the measured exponents are consistent with creation of C$_2$ via a three-photon process. As can be seen, there is a tendency toward lower exponents at longer wavelengths. This suggests that the path followed in the creation of C$_2$ (or one of multiple paths) at longer wavelengths is either rate-limited by two-photon processes or involves a step whereby irradiance-dependent loss mechanisms, such as photo-ionization, saturation, or stimulated emission, are not insignificant.

The structure of the C$_2$H$_2$ excitation spectrum changes significantly at higher jet temperatures, as shown in Figs. 8a and 8b. To compare relative signal intensities as closely as possible, the signals obtained at the higher jet temperatures have been scaled by temperature, which is inversely propor-
tional to the relative \( \text{C}_2 \text{H}_2 \) number density at the jet exit. In addition to the strong absorption bands identified in Watson et al.\(^8\) and Van Craen et al.\(^9\) medium and weak bands that correlate closely with dominant features of the \( \text{C}_2 \text{H}_2 \) excitation spectrum are also identified (in red) in Fig. 8.

At elevated temperature, significant \( \text{C}_2 \) emissions are observed at excitation wavelengths that are nonresonant with \( \text{C}_2 \text{H}_2 \) \( \tilde{A} \)–\( \tilde{X} \) transitions—with the nonresonant signal strength rising at shorter wavelengths. At resonant wavelengths, however, the peak \( \text{C}_2 \) emissions are comparable to those seen in Fig. 5. The overall shape of the low-resolution spectrum in Fig. 8\( a \) suggests that, with increasing temperature, the central portion of the spectrum (46 000–44 000 cm\(^{-1} \)) is enhanced relative to the higher energy portion that dominated Fig. 5. Examination of the particular vibrational transitions involved indicates that this is likely due to the decreased population of the \( v_{\tilde{0}0} = 0 \) and 1 states, characterizing excitation wavenumbers >46 000 cm\(^{-1} \), relative to the \( v_{\tilde{0}4} = 2 \) and 3 states, which are more prevalent in the central portion of the spectrum. The higher-resolution spectrum, in particular, further suggests that the transition probabilities for the \( v_{\tilde{0}4} = 2 \) and 3 states are greater than the probabilities for the \( v_{\tilde{0}4} = 0 \) and 1 states. This observation seems physically plausible because the higher-energy vibrations are more likely to achieve nuclear positions that match the positions of the \( \text{trans} \)-bent \( \tilde{A} \) state more closely.

**SUMMARY AND CONCLUSIONS**

The detection of \( \text{C}_2 \text{H}_2 \) via UV photo-fragmentation, monitoring \( \text{C}_2 \) \( d^3 \Pi_e \)–\( a^3 \Pi_u \) fluorescence, is explored at atmospheric pressure and at temperatures of 295 K, 600 K, and 800 K. Excitation spectra from 210–240 nm and signal dependencies on laser irradiance support the following conclusions:

1. \( \text{C}_2 \) laser-induced fluorescence (LIF) emissions increase steadily as the laser wavelength decreases, but there is no obvious discontinuity that occurs when photon energies fall below \( D_0 \) (\( \text{C}_2 \text{H} + \text{H} \)).

2. \( \text{C}_2 \) emissions correlate closely with the \( \text{C}_2 \text{H}_2 \) \( \tilde{A} \) ← \( \tilde{X} \) absorption probability, indicating that changes in the efficiency of the dissociation processes (\( \text{C}_2 \text{H}_2 \rightarrow \text{C}_2 \text{H} + \text{H} \) or \( \text{C}_2 \text{H}_2 \rightarrow \text{C}_2 + \text{H} \)) play a minor role in enhancing signal levels.

3. The dependency of \( \text{C}_2 \) emissions on irradiance fits well with a power law, with exponents between 2.1 and 3.1 ± 0.3, indicating that the absorption–dissociation path followed may be rate-limited by a two-photon processes or subject to irradiance-dependent loss mechanisms, such as photodissociation, saturation, or stimulated emission.

4. At elevated temperatures, significant \( \text{C}_2 \) emissions are observed at excitation wavelengths that are nonresonant with \( \text{C}_2 \text{H}_2 \) \( \tilde{A} \)–\( \tilde{X} \) transitions.

5. Higher \( \text{C}_2 \) emissions at excitation wavelengths that correspond to \( \text{C}_2 \text{H}_2 \) \( X(\nu'_{\tilde{4}} = 2, 3) \) transitions, rather than \( \nu'_{\tilde{4}} = 0, 1 \) transitions, indicate that transitions originating in \( \text{trans} \)-bent excited states of \( \text{C}_2 \text{H}_2 \) have a greater probability to produce the \( \text{C}_2 \) \( d \) state.

Although resonant excitation near the \( V_{\tilde{5}}^0, V_{\tilde{4}}^1, V_{\tilde{4}}^2, \) and \( V_{\tilde{4}}^4 \) bands at wavelengths less than ~216 nm is advantageous for detection of at \( \text{C}_2 \text{H}_2 \) via photo-fragmentation at 295 K, at higher temperatures, that advantage is rapidly lost because of the higher \( \text{C}_2 \) emissions observed when \( \text{trans} \)-bent initial states of \( \text{C}_2 \text{H}_2 \) are excited (e.g., \( V_{\tilde{5}}^0 \) near 222 nm). Despite rising \( \text{C}_2 \) emissions for nonresonant excitation at higher temperatures, resonant excitation still provides up to a two-fold signal-level improvement over nonresonant excitation at temperatures up to 800 K. The high \( \text{C}_2 \) Swan-band emissions observed with nonresonant excitation do not rule out photo-fragmentation as a viable \( \text{C}_2 \text{H}_2 \) diagnostic technique; nevertheless, they indicate that fluorescent emissions from various \( \text{C}_2 \) systems will be a potential source of interference for a number of combustion diagnostics when \( \text{C}_2 \text{H}_2 \) is present. The present work has focused entirely on the excitation characteristics of \( \text{C}_2 \text{H}_2 \) photo-fragmentation. Additional work at higher temperatures and pressures, characterization the \( \text{C}_2 \) emission intensity variation as a function of \( \text{C}_2 \text{H}_2 \) concentration, and evaluation...
of potential C$_2$ generation from other common combustion species at elevated temperatures and pressures is still required before C$_2$H$_2$ photo-fragmentation can be regarded as a useful diagnostic tool.

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