Laser-induced fluorescence measurements of formaldehyde in a methane/air diffusion flame

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Laser-induced fluorescence has been observed form the formaldehyde $\tilde{A}^1 A_2 - \tilde{X}\, ^1A_1$ electronic transition in a well characterized, laminar methane/air diffusion flame burning at atmospheric pressure. This represents the first optical measurement in flames of naturally occurring formaldehyde, an important intermediate in the oxidation of hydrocarbons. Both 355 nm and tunable dye laser excitation of fluorescence are demonstrated. The observed fluorescence signals are corrected for partition function effects and for estimated collisional quenching rates to obtain relative concentration profiles.

1. Introduction

Laser-induced fluorescence (LIF) is one of the most versatile diagnostic methods used to probe combustion environments, both for species concentrations [1] and for multi-dimensional imaging applications [2]. Numerous atoms and diatomic molecules have been detected in flames with a variety of single-photon and multi-photon fluorescence approaches. However, species-specific data have been obtained for only a handful of polyatomic molecules. Optically accessible fluorescence states are often either unknown or non-existent for even small polyatomics. A recent review of combustion measurements listed only two four-atom species detected via LIF in flames – acetylene and seeded formaldehyde – and no larger species [1]. Here we report the first optical detection of nascent formaldehyde in a flame environment. Our experiments illustrate both the convenience of LIF for flame measurements and the difficulties involved in transforming a fluorescence measurement into a relative concentration profile for a molecule with a large partition function at elevated temperatures.

Formaldehyde is an important intermediate in the oxidation of hydrocarbons [3], particularly in methane combustion where the decomposition of the

methoxy radical ($CH_3O^{\cdot} + M$) and the reactions of $CH_3O^{\cdot} + H^{\cdot}$ and $CH_3 + O:$, O_2, $OH^{\cdot}$, and perhaps $HO_2^{\cdot}$ are involved in its production. Formaldehyde is destroyed by H-atom abstraction reactions with $H^{\cdot}$, $O:$, $OH^{\cdot}$, and $CH_3^{\cdot}$ to form HCO. Calculations of the detailed chemical structure of counterflow and co-flowing methane/air diffusion flames indicate that the peak formaldehyde mole fraction is expected to approach one part per thousand in fuel-rich regions [4,5].

Formaldehyde is well studied spectroscopically. The $\tilde{A}^1 A_2 - \tilde{X}\, ^1A_1$ electronic transition is the subject of a historic paper by Dieke and Kistiakowsky [6] published in 1934. This is perhaps the earliest example of the rotational analysis of a polyatomic molecule [7]. Since then many investigators have contributed to an exhaustive spectroscopic analysis of most of the optically accessible $\tilde{A}-\tilde{X}$ vibronic bands [8]. Because the rotational constants of formaldehyde are relatively large, and given the significant geometry change upon excitation, the rotational structure of the $\tilde{A}-\tilde{X}$ manifold is surprisingly open. The spacing between the individual J, K transitions is often on the order of a few tenths of a wavenumber, and thus can be resolved using conventional pulsed dye lasers.

The accessibility of the $\tilde{A}-\tilde{X}$ transition and the availability of detailed spectroscopic information have fostered numerous investigations of formal-

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dehyde photochemistry. Coupling of the excited A state of formaldehyde to the lowest triplet state and to the dissociative continuum causes interesting photochemical effects, especially a large variation in individual collision-free rovibronic excited state lifetimes [9]. The lifetimes of the A state vibrational bands decrease at higher energies due to predissociation, though not monotonically [10]. Dissociation becomes so fast at excitation wavelengths shorter than 290 nm that fluorescence is undetectable for strong features in the corresponding absorption spectrum. Because of predissociation, the lowest energy vibronically allowed one-photon transition, $\tilde{A}$–$\tilde{X}$ 4_0^1, is the strongest fluorescence band. This band is well suited for diagnostic applications, extending from about 352 to 357 nm.

Formaldehyde measurements in combustion environments have proven to be difficult. Mass spectrometry cannot easily distinguish formaldehyde from ethane at $m/e = 30$ in hydrocarbon flames [11], since their ionization potentials, 10.87 and 12.0 eV [12] respectively, are similar. Some results have been reported in low-pressure, premixed flames [11,13,14]. Gas chromatography provides a clear identification of formaldehyde at the expense of time consuming gas sampling and analysis procedures. Optical detection can furnish an unambiguous assignment, but reported measurements are scarce. Formaldehyde emission has been observed in low-temperature flames [15], and Garland [16] first assigned a broad laser-induced fluorescence spectrum excited at 355 nm to formaldehyde in an investigation of an internal combustion engine [17]. To our knowledge, there exist no prior optical measurements of native formaldehyde under high-temperature flame conditions.

2. Experimental approach and results

The laser-induced fluorescence measurements of formaldehyde have been carried out in a well characterized, laminar methane/air diffusion flame burning at atmospheric pressure. The rectilinear Wolfhard–Parker slot burner and the laser system used in these experiments have been described in detail previously [18–24]. Fig. 1 is a schematic diagram of this burner, the flame stabilizing screens, and
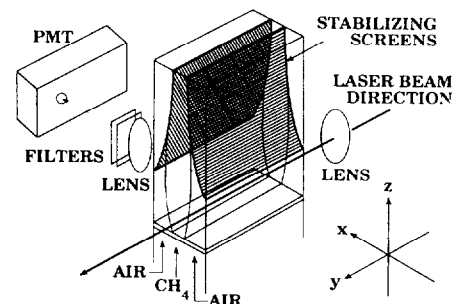

Fig. 1. Schematic diagram of the burner and the optical setup for the laser-induced fluorescence measurements. The flame is stabilized by two curved screens [18].

the optical setup. Methane flows from the center 8 mm wide slot and dry air from the outer two 16 mm slots, producing a diffusion flame with two identical, two-dimensional flame sheets. A long pathlength (40–45 mm) of uniform temperature and chemical composition along the direction of the laser beam facilitates LIF detection. This geometry allows highly precise lateral profile measurements (± 0.1 mm in the x direction, fig. 1) to be made.

Flame conditions were identical to those used previously for profiles of the temperature [18], velocity [18], and various radical and stable species [18–24]. In the present study either a monochromator or a photomultiplier tube/filter combination detected laser-induced fluorescence at 90° to the direction of the laser beam. Initially, 355 nm radiation (15–60 mJ/pulse), produced at 10 Hz by a Molectron [*1] MY35-10 Nd^{3+}:YAG laser and focused with a 100 mm spherical lens, excited the formaldehyde fluorescence. Excitation at 355 nm probes weak rotational transitions within the $\tilde{A}$ $^1A_2$–$\tilde{X}$ $^1A_1$ 4_0^1 vibronic manifold. A 350 nm f/6.8 grating monochromator (GCA/McPherson) collected a fraction of the fluorescence focused with a second 100 mm focal length lens. The monochromator slit width was set to give a bandpass of 2 nm in order to obtain a sufficiently high signal-to-noise ratio.

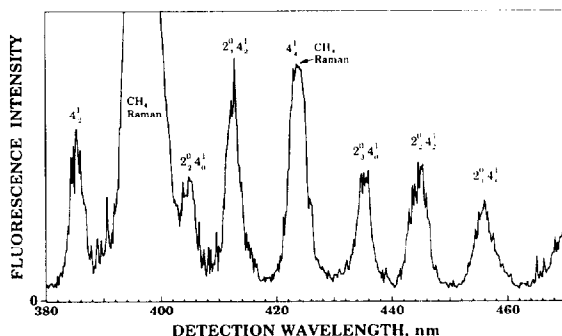Fig. 2 shows the dispersed fluorescence spectrum

Fig. 2. Dispersed fluorescence spectrum of formaldehyde excited by 355 nm light at a height $H = 1$ mm above the burner surface. The vibrational fluorescence bands are labeled along with two methane Raman bands, which are also detected with the flame off while flowing fuel.

from 380–470 nm excited at 355 nm, which provides confirmation of formaldehyde detection by comparison with a literature spectrum taken in a cell [25]. Also present are peaks assigned to methane Raman transitions (at frequency separations of 2914 cm^{-1} and ≈ 4500 cm^{-1}), which are also observed when the flame is not lit, and broadband fluorescence attributed to polycyclic aromatic hydrocarbons (PAH) [18].

Profiles of the formaldehyde fluorescence as a function of lateral flame position (the x direction in fig. 1) were first obtained by translating the burner with the monochromator set to the strongest vibronic band at 412.5 nm. However, a detection bandwidth of 2 nm provides a wavelength interval too large to observe PAH fluorescence independent of formaldehyde LIF. Subtraction of off-resonance signals from on-resonance data yielded formaldehyde profiles which were biased toward low-temperature regions. In order to better discriminate against this background PAH fluorescence, dye laser excitation of formaldehyde between 350 and 355 nm was utilized.

The dye laser experiments employed 0.2–0.9 mJ pulses of ultraviolet light with a bandwidth of ≈ 0.5 cm^{-1}. A 100 mm spherical lens focused the incident light to $a \approx 0.1$ mm diameter spot at the center (along the y direction in fig. 1) of the CH_4/air flame. For greater sensitivity a photomultiplier tube with two filters, Corning GG-395 long pass and Corion LS-550 short pass, detected the formaldehyde LIF with an

overall bandpass of 155 nm. Fig. 3 shows a portion of the K-resolved excitation spectrum of formaldehyde obtained at a height (H) of 1 mm above the burner, with partial J resolution. Assignment of the spectrum is based on constants from the literature [8] and a calculation of the asymmetric top levels with a NIST computer program [26]. Reference to tables in Dieke and Kistiakowsky [6], which list transition energies for $K'' = 3$ and higher, confirmed individual transitions.

The most prominent feature in the spectrum shown in fig. 3 is the $^{R}R_3$ bandhead at 28370.5 cm^{-1}. Here the notation is that for a symmetric top transition, although formaldehyde is a slightly asymmetric rotor. The left superscript labels the change in the K quantum number, the change in J is indicated at the center, and the right subscript denotes K''. For example, $^{R}R_3(9)$ denotes $\Delta K = +1$, $\Delta J = +1$, $K'' = 3$, and $J'' = 9$. Tuning to this bandhead provided maximum fluorescence intensity for measuring on-resonance profiles. Off-resonance profiles were taken by tuning the laser frequency just to the blue at 28371.5 cm^{-1}. At this frequency there is still a small contribution from weak formaldehyde rotational lines (less than 1 part in 30 relative to the background PAH fluorescence). Fig. 4 presents the profile data, obtained with the laser wavelength tuned on and off resonance, for three heights in the flame. These measurements involved averaging 20 laser shots per position and taking points every 0.2 mm
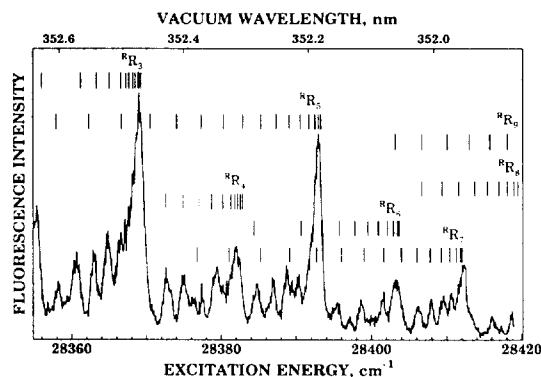

Fig. 3. Partially rotationally resolved fluorescence of the 4_0^1 vibronic band of the $\tilde{A}\,^1A_2-\tilde{X}\,^1A_1$ transition in formaldehyde obtained at a height $H = 1$ mm above the burner surface using dye laser excitation. Rotational ladders are assigned using constants from ref. [8] and line positions from ref. [6].
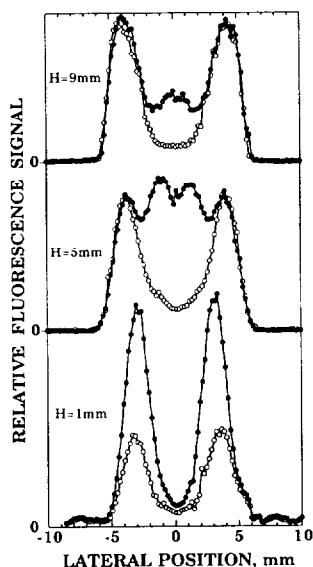
Fig. 4. Formaldehyde LIF profiles obtained using dye laser excitation and measured at heights of 1, 5 and 9 mm above the burner as a function of lateral flame position. The data are shown with the laser tuned to resonance with the $^RR_3$ bandhead at 28370.5 cm^{-1} (solid symbols) and off-resonance at 28371.5 cm^{-1} (open symbols). The zero signal levels are indicated.

across the burner. Laser power measurements were obtained simultaneously. The laser power stability was less than optimal, varying by about 20% through a set of profiles collected at heights from 1 to 11 mm above the burner in 2 mm increments. Although formaldehyde fluorescence increased linearly with laser power (see below), the PAH fluorescence signal was saturated under our experimental conditions. Thus, subtraction of off-resonance from on-resonance profiles was optimized when the data were obtained with constant laser intensities as identical as possible at each height above the burner.

The accuracy of the subtracted fluorescence profiles depends upon equal laser fluence at all of the measured points and upon the extent to which the PAH background can be removed. The symmetry in the LIF signals about the burner centerline indicates that the formaldehyde fluorescence is not being absorbed by the flame. Any attenuation of the incident laser light was below detectable limits (< 1%). The background PAH fluorescence profiles were insensitive to the excitation wavelength in the 352–357 nm region. No evidence for the photolytic produc-

tion of formaldehyde was observed in these experiments, i.e. the shape of the profiles did not depend upon the laser intensity.

The strongest formaldehyde LIF signals are observed low in the flame, where coincidently the nonresonant PAH background LIF signals are small. At higher flame positions, for example in the $H = 7$–11 mm region, the observed formaldehyde signal decreases while the background from PAH fluorescence rises dramatically, as seen in prior work on this flame [18,20,23]. The most successful method of reducing the PAH background contribution was to increase the incident laser intensity as much as possible. Qualitative tests of the linearity of the fluorescence signal with laser power showed that the PAH signal was saturated at a few tenths of a millijoule per pulse, whereas formaldehyde fluorescence remained linear up to the highest obtainable dye laser intensities (≈ 1.5 mJ/pulse). This linearity of the formaldehyde fluorescence at high incident laser intensities is due to a combination of a low intrinsic probability for the $\tilde{A}$-$\tilde{X}$ transition (the radiative lifetime is ≈ 3.1 µs [27]) and rapid rotational energy transfer in the excited electronic state [28]. The formaldehyde signal versus intensity results can be compared to previous work on the easily saturable $A\,^2\Sigma^+$-$X\,^2\Pi^+$ OH$^-$ transition, performed under similar laser and flame conditions. Optical saturation of the $\tilde{A}\,^1A_2$-$\tilde{X}\,^1A_1$ transition of formaldehyde is expected to require at least a 100-fold higher intensity than this OH$^-$ transition [29].

Determination of a relative concentration profile from the observed net LIF formaldehyde profile data requires two corrections. These include compensation for the variation of the collisional quenching rate with flame position and the Boltzmann population of the ground rotational levels involved in the $^RR_3$ bandhead (141 and 160 cm^{-1} above the rotationless energy of the X state). The latter is by far the larger correction, since the formaldehyde partition function varies rapidly with temperature. Cline and Varghese [30] have pointed out how strongly the partition function lowers estimated detection limits for formaldehyde at elevated temperatures. Using previously measured temperature profiles [18], the formaldehyde partition function has been calculated with a statistical mechanical formulation [31]. At higher temperatures the partition function effects re-

duce the observed LIF signals, since a greater number of quantum levels are energetically accessible.

Collisional quenching cross sections have not been measured for formaldehyde at elevated temperatures. A $1/\sqrt{T}$ correction has been made to account for the overall collision rate, which varies strongly across the CH_4/air diffusion flame due to large temperature changes. This may be a poor approximation to the actual quenching rate, since the chemical composition changes rapidly across the formaldehyde profile [18]. Thus, the accuracy of the derived concentration profiles for formaldehyde is limited by the estimated quenching corrections. Quenching considerations act to boost the observed LIF signal in high-temperature regions, since the quenching rate is expected to be lower. Fig. 5 presents a typical measurement at $H = 5$ mm above the burner; the net fluorescence signal, the temperature, the various correction factors, and the resulting relative formaldehyde number density profile are shown.

As is evident in figs. 4 and 5, formaldehyde LIF signals appear only in rich flame regions, inside the positions of the temperature maxima. At higher flame positions the formaldehyde signal is detectable only near the burner centerline. In the region where the PAH interference is largest, significant concentrations of formaldehyde could be present and not detected in these experiments, primarily due to the partition function dilution of the LIF signal. For example, at $H = 5$ mm we estimate that at the location of maximum PAH fluorescence ($x = \pm 4$ mm) up to 25% of the centerline formaldehyde concentration would be difficult to differentiate from the PAH background, assuming that the quenching and partition function corrections are accurate. Nonetheless, there appears to be an overall accumulation of formaldehyde along the centerline, with a corresponding decrease near the high-temperature reaction zones. At $H = 3$ mm above the burner, the formaldehyde fluorescence can be detected at temperatures up to 1600 K, but at $H = 9$ mm it is observable only up to 980 K. In the region of $H = 3$ to 9 mm the PAH interference increases by only a factor of 2 and thus cannot account for the loss of formaldehyde signal at high temperatures. No other intermediate species detected in this flame (e.g., acetylene, benzene, and CO) exhibits such a rapid
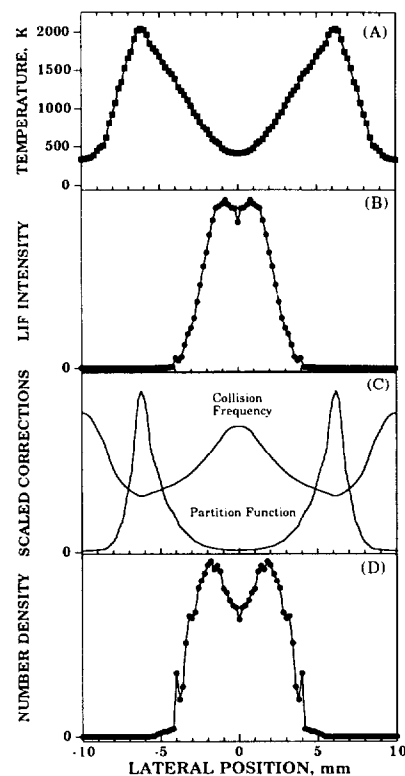

Fig. 5. Temperature, net formaldehyde LIF signal, corrections, and the resulting relative formaldehyde number density at a height of 5 mm above the burner. (A) Radiation-corrected thermocouple temperature measurements [18]. (B) Net background-subtracted formaldehyde LIF profile with subtraction noise at lateral positions of 4–6 mm from the burner centerline omitted. (C) Arbitrarily scaled multiplicative correction factors used to account for the effects of collisional quenching and partition function dilution of the observed signal in high-temperature regions. (D) Relative formaldehyde number density profile determined from multiplying the net LIF signal by the correction factors. All of the data have been symmetrized by averaging about the burner centerline.

accumulation along the centerline [18].

3. Discussion

Laser-induced fluorescence from formaldehyde is readily observable in a CH_4/air diffusion flame close to the burner surface. The LIF signals are reduced at high flame temperatures due to partition function effects, and at higher flame heights, corresponding to later times, the observed formaldehyde profiles be-

come considerably narrower. Part of the explanation for this behavior concerns the interference from broadband PAH fluorescence, which increases rapidly with increasing height above the burner (fig. 4; [18,20,23]). However, interference from this PAH fluorescence and a gradual rise in the flame temperatures in rich regions with increasing height would not seem sufficient to explain the lack of detectable formaldehyde fluorescence near the high-temperature reaction zones. Our data suggest that a major chemical source of formaldehyde exists low in the flame and that the rate of formation of formaldehyde is reduced at higher flame positions. One of the production routes for formaldehyde, the reaction of the methyl radical with O_2 to give $CH_3O^.$, may be enhanced close to the burner, where some O_2 penetration occurs [24]. Once formed, the convective streamlines carry formaldehyde toward the burner centerline [18], where temperatures are cooler and radical concentrations are negligible. As a result, the formaldehyde concentration can build up in rich flame regions where there are no chemical sinks.

Smooke et al. have carried out a detailed computation of the chemical structure of an axisymmetric, co-flowing CH_4/air diffusion flame [5], which shows that the peak concentrations of both the methyl radical and the formaldehyde lie close to the burner surface. In addition, the spatial evolution of the methyl radical and formaldehyde concentrations are closely parallel, suggesting that the dominant formaldehyde formation route involves CH_3. Unfortunately, the limited spatial extent of our relative concentration profiles for formaldehyde precludes both a meaningful calculation of overall production and destruction rates and a detailed reaction path analysis. In particular, at the intermediate flame heights ($H=7-11$ mm) where these analyses have been carried out previously in this flame [20,23,32–34] the formaldehyde concentration data do not overlap the profiles of the major radicals $H^.$ [21], O: [21], and $OH^.$ [20]. Analysis of the chemical roles of formaldehyde must await improved concentration measurements. A higher power and more stable laser source would yield better LIF measurements of formaldehyde near the high-temperature reaction zones. It is also possible that multiphoton ionization [35] or tunable diode laser diagnostics may provide enhanced sensitivities. Gas chromatographic mea-

surements would yield quantitative formaldehyde data and could be used to test the accuracy of our corrections to the LIF measurements.

4. Conclusions

We have observed the 4_0^1 vibronic band of the $\tilde{A}\,^1A_2 - \tilde{X}\,^1A_1$ transition of formaldehyde via laser-induced fluorescence near 353 nm in a CH_4/air diffusion flame burning at atmospheric pressure. This band shows promise for diagnostic applications in combustion conditions, since the LIF signal is sufficiently strong to carry out two-dimensional imaging experiments. Formaldehyde fluorescence is easily recognizable in a CH_4/air flame and would likely be detectable in other hydrocarbon flames; the required near-ultraviolet wavelengths are widely accessible with conventional pulsed dye laser systems. Identification of formaldehyde is also readily accomplished with simply the third harmonic from a Nd^{3+}:YAG laser at 355 nm. The most significant problems in making profile measurements are the interferences from PAH fluorescence and the large partition function dilution of the observed signal which occurs at flame temperatures.

References

[1] D.R. Crosley, Combustion Flame 78 (1989) 153.

[2] R.K. Hanson, 21st International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1986) p. 1677.

[3] J. Warnatz, in: Combustion chemistry, ed. W.C. Gardiner Jr. (Springer, Berlin, 1984) ch. 5.

[4] I.K. Puri, K. Seshadri, M.D. Smooke and D.E. Keyes, Combustion Sci. Technol. 56 (1987) 1.

[5] M.D. Smooke, R.E. Mitchell and D.E. Keyes, Combustion Sci. Technol. 67 (1989) 85.

[6] G.H. Dieke and G.B. Kistiakowsky, Phys. Rev. 45 (1934) 4.

[7] G. Herzberg, Molecular spectra and molecular structure, Vol. 3. Electronic spectra and electronic structure of polyatomic molecules (Krieger, New York, 1991).

[8] D.J. Clouthier and D.A. Ramsay, Ann. Rev. Phys. Chem. 34 (1983) 31, and references therein.

[9] C.B. Moore and J.C. Weisshaar, Ann. Rev. Phys. Chem. 34 (1983) 525, and references therein.

[10] R.G. Miller and E.K.C. Lee, J. Chem. Phys. 68 (1978) 4448.

[11] J.D. Bittner, D.Sc. Dissertation, Massachusetts Institute of Technology (1981).

[12] R.D. Levin and S.G. Lias, Ionization Potential and Appearance Potential Measurements, 1971–1981, NSRDS-NBS circular No. 71 (US GPO, Washington, 1982).

[13] J. Peeters and G. Mahnen, 14th International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1973) p. 133.

[14] P.R. Westmoreland, J.B. Howard and J.P. Longwell, 21st International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1986) ch. 773.

[15] R.W.B. Pearce and A.G. Gaydon, The identification of molecular spectra, 4th Ed. (Chapman and Hall, London, 1976), and references therein.

[16] N.L. Garland, SRI International Report MP 84-033 (1984).

[17] J.R. Smith, R.M. Green, C.K. Westbrook and W.J. Pitz, 20th International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1984) p. 91.

[18] K.C. Smyth, J.H. Miller, R.C. Dorfman, W.G. Mallard and R.J. Santoro, Combustion Flame 62 (1985) 157.

[19] K.C. Smyth and P.H. Taylor, Chem. Phys. Letters 122 (1985) 518.

[20] K.C. Smyth, P.J.H. Tjossem, A. Hamins and J.H. Miller, Combustion Flame 79 (1990) 366.

[21] K.C. Smyth and P.J.H. Tjossem, 23rd International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1990) p. 1829.

[22] K.C. Smyth and P.J.H. Tjossem, Appl. Opt. 29 (1990) 4891.

[23] T.S. Norton and K.C. Smyth, Combustion Sci. Technol. 76 (1991) 1.

[24] T.S. Norton, K.C. Smyth, J.H. Miller and M.D. Smooke, Combustion Sci. Technol., in press.

[25] K. Shibuya, D.L. Holtermann, J.R. Peacock and E.K.C. Lee, J. Phys. Chem. 83 (1979) 940.

[26] A. Maki, FORTRAN program ASYM82, unpublished.

[27] J.C. Weisshaar and C.B. Moore, J. Chem. Phys. 72 (1980) 5415.

[28] P.H. Vaccaro, F. Temps, S. Halle, J.L. Kinsey and R.W. Field, J. Chem. Phys. 88 (1988) 4819.

[29] J.I. Steinfeld, Molecules and radiation: An introduction to modern molecular spectroscopy (MIT Press, Cambridge, 1989) ch. 11.

[30] D.S. Cline and P.L. Varghese, 23rd International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1990) p. 1861.

[31] R.S. Berry, S.A. Rice and J. Ross, Physical chemistry (Wiley, New York, 1980) ch. 21.5.

[32] J.H. Miller, W.G. Mallard and K.C. Smyth, 21st International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1986) p. 1057.

[33] J.H. Miller and P.H. Taylor, Combustion Sci. and Technol. 52 (1987) 139.

[34] K.C. Smyth and J.H. Miller, Science 236 (1987) 1540.

[35] D.S. Bomse and S. Dougal, Laser Chem. 7 (1987) 35.