Laser-induced fluorescence of formaldehyde hot bands in flames

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Laser-induced fluorescence and excitation spectra of formaldehyde in the $A-X \, 4^10$ band at 370 nm are recorded in the primary flame front of a Bunsen flame. An examination of partition functions shows that this excitation can minimize temperature bias for formaldehyde in situ diagnostic measurements.

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1. Introduction

Formaldehyde is an important intermediate in hydrocarbon combustion, formed by the initial oxidation reaction $\text{CH}_3 + \text{O}$, in low-temperature, knock, and methanol combustion, in which it is produced by $\text{CH}_3\text{O}$ decomposition, and as a toxic emission from incomplete combustion.\(^1\) Detection of formaldehyde in flames by laser-induced fluorescence (LIF) has been accomplished by excitation of the strong $A-X \, 4^10$ vibronic band at 355 nm, as demonstrated in a diffusion flame.\(^2\) The spectroscopy of this system is well studied and features strong progressions in both absorption and fluorescence involving $v_4$, which is the out-of-plane $\text{CH}_2$ bend formerly labeled $v_6$, and $v_2$, the carbonyl stretch.\(^3\) The origin band is forbidden, and predissociation of higher-lying excited-state levels reduces fluorescence yields for excitation below 320 nm.

The partition function of formaldehyde varies significantly with temperature, which complicates the interpretation of LIF measurements of this polyatomic molecule in flames, which typically excite the $4^10$ band.\(^2,4\) Models of flame chemistry predict the presence of significant amounts of formaldehyde over a very large temperature range, 700–1800 K. The large temperature variation of the thermal population of the identifiable level of the molecule excited by the LIF laser produces large differences in the fluorescence intensity for a given formaldehyde number density. Thus, even qualitative imaging results that excite the $4^10$ band require some knowledge of the temperature field for interpretation of the measurements. Although one may empirically locate wavelengths within the $4^10$ spectrum that preferentially excite hot rather than cold formaldehyde,\(^4\) actually determining the temperature dependence is another matter. This paper describes a successful alternative LIF hot-band excitation scheme designed to minimize the difficulties of temperature variation of the population in the excited level. An examination of vibrational-state populations and vibronic band strengths suggests that excitation of the $4^10$ band at 370 nm ($v_4' = 1167 \text{ cm}^{-1}$) will mitigate these difficulties.

An atmospheric-pressure methane–air Bunsen flame was probed in the premixed inner-cone region (1.65-cm burner tube diameter, 7.2-standard liters/min flow, $(\Phi = 1.36)$ by a 0.02-cm-diameter tunable dye laser beam (0.2 cm$^{-1}$). Fluorescence was detected through a long-pass filter (>380 nm) for excitation scans or through a 0.27-m monochromator (0.25-nm resolution) for fluorescence scans, by use of a CCD camera. This configuration is described in imaging studies of formaldehyde and CH in Bunsen flames.\(^5\)

Figure 1 shows an excitation spectrum taken at the location of the peak formaldehyde LIF in the inner cone of the flame. The formaldehyde appears inside the inner flame cone prior to the appearance of CH. Note that one can also image CH by LIF in this flame...
by exciting transitions of the \( B - X (1,0) \) band, which are in the same spectral range as the \( A - X \) excitation of \( \text{CH}_2\text{O} \) in the \( 4_{1}^{0} \) band. The constants and the spectrum of the \( 4_{1}^{0} \) band are well known, and the matching assignments shown in the figure clearly identify this excitation. The expected \( K \) subband heads of alternating intensity are identified in the top graph, and the higher-resolution presentation at the bottom illustrates a match to individual line assignments and the structure of the \( K(2) \) \( R \) head. Note from the top graph, in which the zero of intensity is not suppressed, the existence of an underlying quasi continuum, which is typical of the LIF of polyatomics that we have observed in flames. This quasi-continuum is due to additional higher-hot-band and high-rotational-level excitations, as well as any Raman signal, laser scatter, or interfering LIF from other species. The quasi-continuum is caused by the Boltzmann factor divided by the appropriate partition function. Results for temperature dependence are given in Table 1. The first two rows compare the vibrational-level populations (determined by state count) for the ground level and for one vibrational quantum in \( v_4 \), the level excited in this study. The last column shows the ratio of the maximum to minimum values over the temperature range in which formaldehyde is found in flames (700–1800 K) and thus how this dependence is much less for the \( 0_{1}^{0} \) hot-band excitation, although at the sacrifice of total population and thus the most likely LIF intensity. For the next highest hot-band excitation, \( 2_{1}^{0} 4_{0}^{1} \), the range increases to 2.33 but is very flat across the 1000–1800-K range.

The rotational feature to be excited and the temperature dependence of its population must also be considered. Since the \( K \) subband heads of the near-symmetric top provide the most intensity and background contrast in the LIF spectrum, these

Fig. 1. Formaldehyde LIF excitation spectrum, with broadband fluorescence detection, in an atmospheric-pressure methane–air Bunsen flame. Rotational assignments in the \( A - X 4_{1}^{0} \) band are shown in the (bottom) enlargement of the \( K^* = 2 \) subband region at higher resolution.

Fig. 2. Formaldehyde-dispersed fluorescence spectrum following laser excitation of the \( A \)-state ground vibrational level in an atmospheric-pressure methane–air Bunsen flame by use of the \( 4_{1}^{0} K = 3 \to 2 \) \( R(6) \) transition. The likely fluorescing vibronic transitions are labeled.
alternatives are further explored in the table. The relative population fractions versus temperature for three values of \(K\), including the vibrational factor, are given in the table. Although rotational consideration introduces added bias, many of the bandhead choices are acceptable. \(K = 5\) population values are optimum, but the bandhead intensities become weaker. A similar analysis and result applies to rovibronic levels of the next hot band, \(2^1 \tilde{0} \rightarrow 3^1 \tilde{78} \text{nm}\), with a lower optimum \(K\). The \(A-X\) excitation from \(2^1 \tilde{40}\) is a weaker transition and has a smaller thermal population.

In addition, any variation in quenching rate over the temperature range will introduce additional dependence. Density, composition, and collision rate changes produce a variation in quenching rate. If we make the simplest, unjustified assumption that the quenching cross section is constant, the net quenching rate will vary as \(T^1\), which favors high-temperature detection by a factor of \(T^{1/2}\). If mole fraction is desired instead of concentration, a factor of \(T^{-1}\) is introduced. The resulting computed temperature bias factors are shown for \(K = 6\) in the last two rows of Table 1. The combination of temperature variation of the initial-state population and that assumed for quenching predicts the LIF signal could vary by a factor of 2 for a given formaldehyde number density and 5 for a given mole fraction over the temperature range 700–1800 K.

To obtain Bunsen flame planar LIF images we excited formaldehyde at the \(A-X 4^1 \tilde{0} \rightarrow 6^1 \tilde{K} = 7 \leftarrow 6\) maximum, using a 0.025 cm \(^2\) 2.0 cm sheet of laser light (0.4 mJ/pulse). Filtered fluorescence with wavelengths longer than 380 nm was imaged upon a gated intensified CCD camera (Princeton Instruments ICCD-576G/RBT) and averaged over 2500 laser shots. We took a second image with the laser tuned just beyond the blue end of the subband head and subtracted it from the first image to remove interference from nonresonant fluorescence, Raman scattering, flame emissions, and laser scatter. (Some noise, including a faint trace of the optical flame-front emission outside the formaldehyde signal of the \(\Phi = 1.36\) flame cone, can be seen as a result of imperfect subtraction.) The images are also corrected for laser-sheet and detector-array inhomogeneities by normalization to a Rayleigh scattering image and smoothed by binning over \(2 \times 2\) pixels. The spatial resolution is \(\sim 0.02\) cm.

Results for \(\Phi = 1.36\) and \(\Phi = 3.0\) inner-cone stoichiometry flames with equal total flow rates are shown in Fig. 3. The signal levels are quite uniform in intensity and width along the flame cone and are associated only with the premixed flame-front area. The peak formaldehyde LIF intensity for the \(\Phi = 3.0\) flame is \(\sim 45\%\) that for \(\Phi = 1.36\), although the integrated intensity is \(60\%\) larger, reflecting the increased width that is evident in Fig. 3. Although the

### Table 1. Temperature Dependence of the Formaldehyde Populations

<table>
<thead>
<tr>
<th>Level</th>
<th>Temperature (K)</th>
<th>300</th>
<th>500</th>
<th>700</th>
<th>1000</th>
<th>1400</th>
<th>1800</th>
<th>Range 700–1800 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibrationless</td>
<td></td>
<td>0.99</td>
<td>0.92</td>
<td>0.77</td>
<td>0.53</td>
<td>0.30</td>
<td>0.16</td>
<td>4.7</td>
</tr>
<tr>
<td>(v'=4, K = 1)</td>
<td></td>
<td>0.004</td>
<td>0.032</td>
<td>0.070</td>
<td>0.099</td>
<td>0.089</td>
<td>0.064</td>
<td>1.55</td>
</tr>
<tr>
<td>(v'=4, K = 2, J = 6)</td>
<td></td>
<td>0.019</td>
<td>0.090</td>
<td>0.128</td>
<td>0.111</td>
<td>0.062</td>
<td>0.031</td>
<td>4.09</td>
</tr>
<tr>
<td>(v'=4, K = 6, J = 6)</td>
<td></td>
<td>0.0409</td>
<td>0.381</td>
<td>0.671</td>
<td>0.688</td>
<td>0.430</td>
<td>0.230</td>
<td>3.15</td>
</tr>
<tr>
<td>(v'=4, K = 10, J = 10)</td>
<td></td>
<td>0.007</td>
<td>0.185</td>
<td>0.536</td>
<td>0.799</td>
<td>0.640</td>
<td>0.393</td>
<td>2.03</td>
</tr>
<tr>
<td>Quenched (K = 6)</td>
<td></td>
<td>0.032</td>
<td>0.322</td>
<td>0.671</td>
<td>0.821</td>
<td>0.607</td>
<td>0.367</td>
<td>2.23</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>0.075</td>
<td>0.451</td>
<td>0.671</td>
<td>0.575</td>
<td>0.304</td>
<td>0.143</td>
<td>4.72</td>
</tr>
</tbody>
</table>

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![Fig. 3. Planar LIF on-axis images of formaldehyde in Bunsen flames with inner-cone stoichiometries of (bottom) 3.0 and (top) 1.36. Broadband fluorescence was detected beyond 380 nm following excitation at 368.2 nm (\(K = 6\) head), with subtraction of the off-resonance signal excited by the shorter laser wavelength. Zero height is the top of the 16.5-mm-diameter burner tube.](image_url)
total flows are the same, the richer flame has a much higher cone height (22 cm) and thus a much larger flame-front area. The premixed flame speed of the richer flame, as indicated by the flow rate through the flame front, is much slower, and a longer time for combustion is reflected in the wider distribution that was observed for the partially oxidized intermediate formaldehyde.

In conclusion, LIF detection of formaldehyde in flames by use of excitation at one of the higher $K$ subband heads of the $A-X\,^4\Pi$ band provides an efficient method of imaging this important intermediate while reducing temperature bias in the measurement over a wide range.

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References


