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Authors
Peterson, R.
Ikegawa, M.
Lucas, D.

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April 1985
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Measurement of Combustion Species by Electron Impact Fluorescence

R. Peterson*, M. Ikegawa#, and D. Lucas

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Joint Technical Meeting of the Central and Western States Sections of
The Combustion Institute

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*Present Address: Internal Ballistics Division, Ballistic Research
Laboratory, Aberdeen Proving Ground, MD 21005

#Present Address: Hitachi, Ltd. Mechanical Engineering Research
Laboratory, 502, Kandatsu-Machi, Tsuchiura-shi, Ibaraki, 300, Japan

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ABSTRACT

We have developed a new diagnostic technique for the time-resolved measurement of chemical species important in combustion systems. The method is based on electron impact fluorescence from atoms and molecules in an expanding free jet. Spectra were obtained from the electron impact of CO, CO₂, CH₄, O₂, air, and Ar at different electron energies in a steady-state system. We have demonstrated the application of the technique for monitoring transient events by continuously measuring a single frequency unique to a particular species during combustion of spark-ignited methane/oxygen/argon mixtures. Advantages of the technique are discussed, and include fast temporal response, high sensitivity and selectivity, simultaneous multi-species detection, and low equipment costs.
INTRODUCTION

Molecular beam mass spectroscopy (MBMS) has proven to be a valuable tool for the study of combustion systems. Its application to steady-state systems has yielded answers to many questions concerning the chemistry of flames and reacting systems\(^\text{1-4}\). Transient systems have also been studied, but with less success due to inherent problems associated with sampling and interpretation of results\(^\text{5-8}\).

The limitations of direct sampling MBMS have been discussed by Smith\(^\text{9}\), and we have provided detailed theoretical modeling and experimental results of transient combustion\(^\text{10-12}\). During this research we were able to identify areas important in the study of transient combustion, and began to develop ideas to improve the detection of molecules when molecular beam sampling techniques are applied to time varying combustion events.

We are investigating the coupling of direct sampling with electron impact fluorescence (EIF). EIF has been used by a number of researchers to investigate the spectrum of various atoms and molecules cooled in a supersonic beam\(^\text{13-16}\). Their results led us to believe that EIF could be used to study non-steady combustion with improved species selectivity and temporal resolution.

In this paper we present spectra of several species of interest in combustion obtained in steady-state experiments, and time-resolved records from spark-ignited methane/oxygen/argon mixtures at two different equivalence ratios. These experiments show the feasibility of the technique, and we discuss how it can be used to further our understanding of transient combustion phenomena.
EXPERIMENT

The three-stage molecular beam system described previously\textsuperscript{10} was modified to allow installation of an electron gun assembly, free jet source, and a window for optical access. A schematic of the apparatus is shown in Fig. 1. The components were mounted in the second stage, pumped by a Varian 6\textquotedbl oil diffusion pump. The existing molecular beam skimmer was removed to allow additional pumping by the NRC 10\textquotedbl oil diffusion pump in the first stage. The third stage pump was not used. Background and operating pressures were $3 \times 10^{-5}$ torr and $10^{-3}$ to $10^{-4}$ torr, respectively.

Two different source arrangements were employed. The steady-state source consisted of a 0.3 cm diameter pyrex tube with a small piece of stainless steel foil glued to its end. An orifice was fabricated by indenting the foil with a needle followed by grinding with silicon carbide powder. This method can produce hole diameters as small as 50 micrometers. We have produced beams with Mach numbers of $>15$ using argon at 1.0 atm using similar sources\textsuperscript{10}.

The second source arrangement, used for the transient combustion experiments, was a quartz cell with a volume of 11.3 cm$^3$. The cell contained two tungsten electrodes, a gas feed tube, and a quartz sampling probe. The source was conical with a 200 micrometer diameter orifice at its apex. This type of probe, used in our previous molecular beam studies, has been shown to sample reacting mixtures with no apparent perturbations\textsuperscript{11,12}. 

2
The electron gun assembly was fabricated from stainless steel, quartz, and unfired ceramic. Electrons, produced by heating a tungsten filament with a regulated a.c. power supply, were accelerated by applying a negative voltage to both the filament and a plate behind the filament. The electrons passed through a 0.4 x 0.9 cm aperture cut into a plate which was held at ground potential. Focusing or alignment lenses were not used in these experiments. The electron current was measured with a Faraday cup located approximately 2.5 cm from the aperture plate. The spread in the electron energy and the spatial distribution of the beam were not determined. Beam currents of up to 1.0 mamp were measured with no free jet present.

Gas mixtures were prepared by flowing individual gases through calibrated flowmeters into a mixing tube filled with pyrex spheres. Argon, methane, nitrogen, and oxygen were obtained from the Lawrence Berkeley Laboratory supplies. Carbon dioxide and carbon monoxide were obtained from the Matheson Corp. All gases were use without further purification.

Combustion was initiated by a spark discharge in mixtures of CH$_4$, O$_2$, and Ar. A 4 uf capacitor, charged to 2.5 kV, was discharged through a high Systems, Inc. 10:1 trigger transformer, with the resulting spark lasting ~100 usec. A typical mixture was CH$_4$:O$_2$:Ar = 1:2.6:10.4, initially at a pressure of 0.5 atm.

Light emission orthogonal to the free jet and electron beam was observed through a quartz window in the vacuum chamber. A McPherson 0.3 m scanning monochromator and a Hamamatsu R955 photomultiplier tube were used to disperse and detect the fluorescence. Slit widths were 0.5 nm in the steady-state experiments and 1.5 nm in the combustion experiments. PMT signals were amplified by a Pacific Photometric 60A-2 amplifier.
Spectra were recorded on a Linear strip chart recorder. Transient signals were processed using a DEC microcomputer-CAMAC crate system described previously. A typical run involved digitizing 500 points at a rate of 50kHz.

RESULTS

1. Steady-State Experiments

Steady-state experiments were conducted using pure gases to obtain a fluorescence spectrum from Ar, O₂, CO₂, CO, CH₄, and for air. All of these species produced light in the visible portion of the spectrum, with the characteristic shape of an expanding free jet easily seen in a darkened room. While the chemical species responsible for the emission is most likely a singly charged ion, we will use the parent compound name for identification purposes. The origin of the fluorescence will be discussed later.

Electron impact fluorescence spectra for these species obtained with a constant 0.5 nm bandpass and at various electron energies are shown in Fig. 2 through 7. Spectra of a particular species recorded at different electron energies showed no significant differences except for the intensity of the peaks. This was found for the species studied over a range of energies from 60 to 390 electron volts.

Plots of a single fluorescence peak intensity as a function of electron energy were used to determine the optimal operating conditions. The plot for the 430.1 nm band arising from CH₄ is shown in Fig. 8. The scatter in the data is due mainly to difficulties in maintaining a constant electron current with changing energy. Our results are in
agreement with previous experiments on ionization efficiencies\textsuperscript{17}, and indicate that energies of 100 to 140 electron volts should be used for the detection of stable combustion species.

A plot of fluorescence intensity from CH\textsubscript{4} as a function of electron beam current is shown in Fig. 9. The data were recorded at 430.1 nm, and at an electron energy of 140 volts. The data appear linear, suggesting that only single electron-molecule collisions are responsible for the observed signal. The slight curvature at lower currents is probably due to background light and uncertainties in measuring low electron currents.

2. Transient Combustion Experiments

The spectra from the six species were examined to determine which emission line would yield the strongest signal for a particular species with minimum interference from other species. This wavelength was used in combustion experiments to obtain a time-resolved concentration profile for a single species. A list of the wavelengths used to measure each molecule is presented in Table I.

The combustion cell for the transient experiments had a constant flow of reactants. The initial pressure was approximately 0.5 atm, and no attempt was made to measure the pressure during combustion. Two equivalence ratios were used: 0.7 and 1.1.

Figure 10 shows the long-term time-resolved fluorescence curves arising from three combustion species reacting at an equivalence ratio of 0.7: CO\textsubscript{2}, O\textsubscript{2}, and CH\textsubscript{4}. Each curve has been averaged separately over a number of events: 20 for CO\textsubscript{2}, 111 for O\textsubscript{2}, and 220 for CH\textsubscript{4}. The spark igniter, triggered 90 msec after the start of the data recording, produces a noise spike lasting 1 msec. Growth of the CO\textsubscript{2}, and a decrease in the CH\textsubscript{4} and O\textsubscript{2} occurs in less than 5 msec. The behavior of these signals show
the purging of the combustion cell by fresh reactants. The time needed for replenishment of the reactants is much longer than the observed reaction time; the gas flow thus does not significantly alter the reaction kinetics.

Fluorescence from CO$_2$ at shorter times are shown in Fig. 11 and 12. The equivalence ratio was 0.7 for Fig. 11, and 1.1 for Fig. 12. Both traces are averaged over 20 events. The large noise spike at ~1.7 msec is due to the light associated with the spark discharge. As expected, there is a significant difference in the behavior of each curve, with the CO$_2$ production slower in the rich combustion case. Carbon monoxide measurements (not presented) show an increase followed by a decline when the CO$_2$ begins to grow in the lean case. However, for rich combustion CO grows continuously. Other reactants and products behave as expected for this system.

**DISCUSSION**

1. Species Identification

It should be noted that the fluorescing species is probably not the parent compound. Some of the spectra reported here have been measured and analyzed previously. Important combustion species such as N$_2$, N$_2$O, CO$_2$, and H$_2$O have been studied in supersonic beams$^{14}$, while many other species including CO have been studied by other methods$^{18}$. These efforts have shown that the fluorescing species is usually the singly charged cation of the parent molecule, with some emission due to cracking of the parent (for example, CO$^+$ and CO$_2^+$ from CO$_2$). The situation is similar to mass spectrometry, where ions formed from neutral species are detected, and
care must be taken to insure that the signal observed is indeed proportional to the concentration of the parent compound. We have not attempted to identify the species or state resulting in a particular line. Rather, we present spectra to show the type of emission resulting from a particular compound of interest in combustion, and show how a single species may be monitored in the course of an experiment.

One of the advantages of the free jet expansion is that it cools the molecules and thus reduces the number of lines present in the spectrum. The number of lines present for each species offers a simple check for species interference; by observing one species at several different wavelengths one can eliminate the possibility of overlapping emission by different species.

Emission from unreacting molecules such as argon can be used to follow changes in the density of molecules in the detection region caused by combustion-generated differences in the source conditions. This method has been used successfully in a molecular beam mass spectrometer system\textsuperscript{12}, and should present no additional difficulties here.

2. Transient Combustion

Figures 10, 11, and 12 show that transient combustion events can be followed using electron impact fluorescence. The reaction times observed are reasonable for mixtures of this type, with an initial pressure of 0.5 atm and a spark ignition source located at one end of the cell. Combustion in this cell differs from ideal constant-volume combustion because of the steady flow of reactants. A theoretical modeling of the reaction thus would be very difficult. Our goal was to show the feasibility of using the electron impact fluorescence technique to follow non-steady combustion.
3. Time Resolution

An important question to consider is the ultimate temporal resolution possible while recording a transient combustion event. There are two factors to consider in determining the time resolution possible in our system: the inherent resolution due to the spread in molecular arrival times in the free jet expansion, and the special case of beam overrun in combustion systems where a temperature gradient exists.

We calculated the spread for a 1.0 usec pulse of argon leaving the source at various temperatures and Mach numbers, using standard gas dynamic flow relations for perfect gases. The technique used has been described in detail previously. The distance to the detection region was fixed at 3.0 cm. At 300 K and \( M = 15.0 \), the half-width associated with molecular arrival times is 5 usec. For 2000 K and \( M = 5.0 \), the result is 6 usec. While the results do not include electronic response times and are for an infinitely thin detection region, they do indicate the resolution possible. These values should be compared to those calculated for a conventional molecular beam, where the beam path is usually >20 cm. Similar source conditions result in arrival distribution half-widths of 40 and 47 usec, respectively.

The short path length also greatly improves the ability to make meaningful measurements in systems with rapid increases in temperature. Beam overrun, a term used to describe the effect when molecules sampled from a cool source are overtaken by faster molecules sampled from a hotter source later in the reaction, limits the rate of temperature increase which can be tolerated when sampling combustion species. The rate of temperature increase needed for the critical overrun has been determined by Smith to be inversely proportional to the path length. Our system, with a 3 cm. length, has a critical temperature rate of \( 1 \times 10^7 \) K/sec.
This permits, for example, accurate sampling of atmospheric pressure, stoichiometric methane/air flames.

4. Sensitivity

Another important consideration is the ability of this technique to monitor low concentrations of molecules. Because we did not attempt to optimize the experimental apparatus for maximum signal strength, calculation of the expected radiation flux is useful.

The interaction volume is assumed to be a cylinder 0.2 cm long having the diameter of the electron beam. For mean free paths $>> 1$ cm, the molecules have a excitation impact area

$$A_{im} = 0.2 \left( \frac{\pi}{4} \right) (D_b)^2 n A_{em} \text{ cm}^2,$$

where $D_b$ is the electron beam diameter, $n$ is the density of molecules, and $A_{em}$ is the emission cross section. Dividing by the electron beam cross-sectional area yields the fraction of molecules that will emit: $f = 0.2 n A_{em}$. Multiplying by the electron beam current $I^*$ gives the number of emission events per second,

$$N = 0.2 n A_{ex} I^*.$$

We assume an electron beam current of 0.5 mamp, or $3 \times 10^{15}$ sec$^{-1}$.

The properties of the expanding free jet are calculated using standard gas dynamic relations. The density of molecules 3 cm downstream of a 125 micrometer source is $3.5 \times 10^{13}$ cm$^{-3}$ when the source gas has a specific heat ratio of 1.4 and is at 300 K and 1 atm.

Consider the case of CO$_2$ in the expanding free jet. It has an electron impact induced emission cross section$^{18}$ for the $A^2\Pi_u \rightarrow X^2\Pi_g$ band of approximately $8 \times 10^{-17}$ cm$^2$. In the cold free jet $\sim 10\%$ of the light emitted in this band is at 288 nm. If one assumes a collection efficiency of 10% and a concentration of 100 ppm (0.01%), the rate of
detected photons is $2 \times 10^6$ sec$^{-1}$. For a transient event with a resolution of 10 usec, 20 photons will be detected in this time period. Photon counting techniques permit this rate to be measured easily.

This calculation can be extended to other species, many of which have similar cross-sections. For example, atomic hydrogen, certainly of interest in combustion, has a cross-section of $10^{-17}$ cm$^2$ for the $2p \rightarrow 1s$ transition at 20 ev$^{20}$. Thus it should be possible to measure atomic hydrogen in transient combustion systems at the 100 ppm level. Signal averaging may extend the detection limit into the 1-10 ppm range.

4. Implications for Future Work

Future work will center on improving the experimental technique. A dedicated apparatus will be constructed with improved ion and fluorescence optics. The new apparatus will be equipped with multiple windows for simultaneous detection of two or more species at different wavelengths. Heated sources will also be employed to obtain high temperature calibrations for stable species.

One of our major goals is to extend this technique to measurements of unstable species. Calculations presented in the preceding section indicate that sensitivity should not be a major problem. However, obtaining spectra for some of these molecules might be difficult. Several different approaches to this problem, including low-pressure microwave discharges, continuous plasma jets, and low pressure flames will be used to produce high concentrations of radicals such as OH, O, and H in relatively simple environments. Coupling electron impact fluorescence with other, existing diagnostic methods such as mass spectrometry and laser-induced fluorescence will also be explored.
CONCLUSIONS

We have demonstrated that electron impact fluorescence in a free jet expansion is a useful diagnostic method for the detection of combustion species. We have obtained spectra for several stable molecules important in combustion, and have obtained time-resolved measurements for these molecules in a spark-ignited mixture of methane, oxygen, and argon. Calculations show that this technique is capable of measurements with a temporal resolution of 10 usec, and with enough sensitivity to measure species concentrations in the range of 100 ppm.

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REFERENCES


### TABLE I

Optimum electron impact fluorescence wavelengths for combustion species

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>419.1</td>
<td>2</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>391.0</td>
<td>36</td>
</tr>
<tr>
<td>CO</td>
<td>401.5</td>
<td>11</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>288.3</td>
<td>7</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>430.1</td>
<td>2</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>558.4</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1. Schematic diagram of the electron beam assembly and spark-ignited combustion cell.

Fig. 2. Electron impact fluorescence spectrum of pure CO recorded at a nominal electron energy of 120 volts.

Fig. 3. Electron impact fluorescence spectrum of pure CO\textsubscript{2} recorded at a nominal electron energy of 390 volts.

Fig. 4. Electron impact fluorescence spectrum of pure O\textsubscript{2} recorded at a nominal electron energy of 290 volts.

Fig. 5. Electron impact fluorescence spectrum of pure Ar recorded at a nominal electron energy of 120 volts.

Fig. 6. Electron impact fluorescence spectrum of pure CH\textsubscript{4} recorded at a nominal electron energy of 140 volts.

Fig. 7. Electron impact fluorescence spectrum of air recorded at a nominal electron energy of 120 volts.

Fig. 8. Fluorescence intensity at 430.1 nm as a function of electron energy using pure CH\textsubscript{4} in the free jet.

Fig. 9. Fluorescence intensity as a function of electron beam current for a free jet of CH\textsubscript{4} and an electron energy of 140 volts.

Fig. 10. Time-resolved fluorescence from CO\textsubscript{2}, O\textsubscript{2}, and CH\textsubscript{4} in a spark-ignited mixture of O\textsubscript{2}/CH\textsubscript{4}/Ar at an equivalence ratio of 0.7.

Fig. 11. Time-resolved fluorescence from CO\textsubscript{2} at an equivalence ratio of 0.7.

Fig. 12. Time-resolved fluorescence from CO\textsubscript{2} at an equivalence ratio of 1.1.
$\text{CO}_2$

390 eV

WAVELENGTH (nm)

INTENSITY (A.U.)
Fig. 6
Fig. 9
Fig. 10

CARBON DIOXIDE

OXYGEN

METHANE

TIME (SEC)
CARBON DIOXIDE

INTENSITY (A. U.)

TIME (MSEC)

XBL 853-1766

Fig. 11
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