Laser Raman and Resonance Fluorescence Spectra of Flames

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Summary Laser excited Raman spectra of CO_2, N_2, CH_4, and H_2 in a town-gas–air flame and resonance fluorescent spectra of C_2 radicals have been recorded.

INFORMATION on reactants, mechanisms, and products of combustion processes in dynamic systems is usually based on analyses of gases extracted from flames[1] and spectroscopic studies.[2] Although invaluable as a means of monitoring materials within the combustion zone (*e.g.* by mass spectrometry, or gas phase chromatography) the use of probing techniques is questionable as the introduction of a probe must inevitably disturb the gas flow. The use of cooled probes of sufficiently small diameter will minimise this effect, but some flame quenching may well occur, while fractionation of the quenched, cooled products can occur within the probe, so producing a distorted picture of materials present at any point in the flame. Emission or absorption spectroscopic techniques do not suffer from these defects, but are in turn limited in their spatial resolution properties, *i.e.* emission or absorption can occur from any point in the flame within the optical cone of acceptance of the spectroscopic system. Methods have been devised for improving the effective spatial resolving properties of these techniques but usually involve the use of atypical combustion conditions (*e.g.* flames at low pressures or the use of novel burner geometries). In this preliminary account we show how laser excited spectra, (both Raman and fluorescent) yield information on flame processes. Although the technique will never rival mass spectrometry in sensitivity of detection, it offers an optical probing method with excellent spatial resolution properties.

Laser Raman spectra within flames were excited with a commercial laser Raman spectrometer (Spex 1401) with conventional 90° viewing optics, and a Spectra Physics Model 165 argon ion laser (producing 1·5 W at 488·0 and 514·5 nm). The laser was interrupted by a mechanical chopper at 700 Hz, the output from the photomultiplier (cooled ITT FW 130) being fed to a A.I.M. "Minilock" (MLS 249A) phase sensitive detector. The latter enabled us to discriminate between the flame emissions and the laser excited signal. Photon counting electronics were also used in estimates of total flame emission.

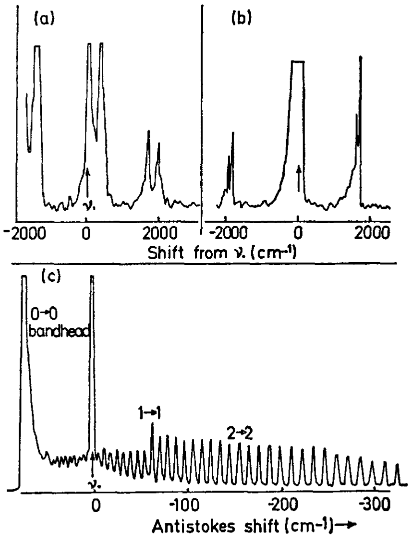

FIGURE. (a) *Low resolution resonance fluorescence spectrum of* C_2 *excited by* $\lambda_0 = 501·7$ nm *radiation.* (b) *Low resolution resonance fluorescence spectrum of* C_2 *excited by* $\lambda_0 = 514·5$ nm *radiation.* (c) *High resolution study of the origin* (0,0) *band of* C_2 *excited by* $\lambda_0 = 514·5$ nm.

Stoicheiometric or slightly fuel rich oxygen–ethylene flames at one atmosphere gave good spectra due to laser excited resonance fluorescence of the species C_2 in the flame. Our findings were that the signal was proportional to laser output, was mixture dependent, and varied in strength throughout the flame. This is as expected for Raman spectra, but the signal was relatively strong compared to the anticipated Raman band intensity, came *only* from the primary reaction zone, varied in intensity and characteristic form using different laser lines (Figure), and was of a complex, band-like structure (Figure).

A high-resolution study of these bands [Figure (c)] yielded data consistent with the formation of C_2 species in the primary reaction zone, *i.e.* in the volume where its concentration is highest under the stated conditions.[2,3] A simple, uncorrected temperature from a consideration of the (0,1) and (1,0) band intensities has yielded a figure of 2600 K, a figure in agreement with that widely accepted[4] for this type of flame.

A study of domestic gas–air diffusion flames yields vibrational Raman spectra characteristic of CO_2, N_2, O_2, CH_4 and rotational lines of H_2. Relative intensities were shifted from the unlit gas–air mixture and varied with mixture strength and position within the flame envelope. With suitable burner geometry no problems are caused by laser focus shifts due to refractive index gradients in the gas flow.

We suggest that both laser excited fluorescent and Raman spectroscopy are potentially powerful tools for the investigation of burning systems under a variety of conditions. Since the light observed has its source in a volume of approximately cylindrical form about 20 μ in diameter × 100 μ in length at the laser focus,[5] this optical probe is capable of great spatial resolving power. The resonance fluorescence phenomenon, limited at present to the C_2 species is, furthermore, highly sensitive, the spectra recorded being due to an estimated concentration of 10^{16} molecules cm^{-3} or less,[6] and from the quality of the spectra a reduction of about three orders of magnitude on this signal would still give meaningful results. Raman spectra in this context are less sensitive but vibrational spectra can be recorded at partial pressures of 1/100 atm. within the flame for CO_2 and N_2 for example.

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[5] J. J. Barrett and N. I. Adams, *J. Opt. Soc. Amer.*, 1968, **58**, 311.

[6] Ref. 4, p. 196 for example.