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The Determination of Temperature in Methane-Air, Propane-Air and Butane-Air Flames Using the Raman Q-Branch Spectra of Nitrogen

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The unresolved Q-branch profiles in the Raman spectra of nitrogen in premixed, laminar, methane-air, propane-air and butane-air flames with lean to stoichiometric fuel-air equivalence ratios have been recorded experimentally and used to determine flame temperatures with a precision of about 1% using an iterative computer program which fitted calculated nitrogen spectra to the experimentally recorded spectra. Axial and radial temperature profiles in these flames are presented and the results compared with calculated adiabatic flame temperatures.

INTRODUCTION

Linear Raman spectroscopy has been shown to be useful for the study of laboratory flame systems and a limited number of such investigations have been reported. Drake and Rosenblatt[1] achieved a precision of 2.5% in the measured temperature of a hydrogen diffusion flame and a methane-air flame using pure rotation Raman spectra; and following the pioneering work of Lapp and Penny[2], Hill[3] and Setchell[4] achieved a precision of about 1% in the measured temperatures of a methane-air flame using the vibration-rotation unresolved Q-branch Raman spectra of nitrogen.

The application of CARS, a non-linear Raman technique, to flame thermometry was pioneered by Taran and co-workers[5] and subsequently developed by them[6,7] and others[8,9,10,11] as a powerful method for the study of flames in hostile environments.

In this paper we report Raman spectroscopic measurements of temperature in pre-mixed, laminar, methane-air, propane-air and butane-air flames with fuel-air equivalence ratios of $\Phi = 0.47$—1.00. Previous vibration-rotation Raman and CARS temperature studies have been made separately on the methane-air[1,3,4,12,13] and propane-air[1,10,14,15,16,17,18] systems but there appear to be no reports in the literature for the butane-air system. From the

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present study it is possible to compare the results for the three fuel-air systems, namely methane-air, propane-air and butane-air, obtained using the same experimental arrangement and identical analytical procedures.

EXPERIMENTAL

A premixed fuel-air burner of length 1 m and internal diameter 1 cm was used with the air flow-rate constant at 3792 cm^3 min^{-1} (equivalent oxygen flow-rate 758 cm^3 min^{-1}). The hydrocarbon fuel flow-rate was varied to meet the requirements for the desired fuel-air equivalence ratio, Φ, defined by

$$\Phi = \frac{\text{theoretical oxygen requirement}}{\text{actual oxygen used}}$$

Raman spectra were recorded at axial intervals of 5 mm and radial intervals of 1 mm in each flame over a range of Φ values between 0.47 and 1.00 using an argon-ion laser with a nominal power of 6 W at 488.0 nm. To enhance the power at the sample a light-trapping illuminator based on the ellipsoidal planospherical mirror design of Hill and Hartley[19] was used. This increased the observed Raman intensity by five times compared to that obtained with a single pass of the laser beam. The length and diameter of the focal cylinder of the multi-passed laser beam in the illuminator were 2 mm and 0.1 mm, respectively. The long axis of the focal cylinder lies in the horizontal plane and was rotated through 90° using a three-mirror image rotator placed before the entrance slit of the spectrometer. The scattered radiation was collected at 90° using an $f/1.2$ camera lens and dispersed using a Spex 1400-II double monochromator operating in the third order with a slit width of 5.3 cm^{-1} and a reciprocal linear dispersion of 10.6 cm^{-1} mm^{-1} at 550.0 nm, the wavelength of the $Q\,(1 \leftarrow 0)$ line of N_2 at $\Delta\nu = 2330$ cm^{-1}.

The scanning of the spectrometer and the acquisition of data were controlled by a Nicolet 1180 system. The data were collected in 256 channels of computer memory and nine scans of the Stokes spectral region, $\Delta\nu$ = 2240—2360 cm^{-1}, were accumulated for each spatial element sampled in the flame. A scan speed of 2.5 cm^{-1} s^{-1} was used and each spectrum of nine accumulated scans took approximately 15 min. to record.

Analysis of the Spectra

The isotropic contribution to the total scattered intensity, $\perp I\,(\pi/2)$, at $(\tilde{\nu}_o - \Delta\tilde{\nu})$ of a Stokes Q-branch vibration-rotation line, $J \leftarrow J$ and $(v + 1) \leftarrow v$, where $J = 0, 1, 2 \ldots$ and $v = 0, 1, 2 \ldots$, is given by

$$\perp I(\pi/2) = C_{iso}\, g_J\, (2J + 1)\, (v + 1)\, (\tilde{\nu}_o - \Delta\tilde{\nu})^4\, Q_r^{-1}\, Q_v^{-1} \exp\{- \left| G\,(v) + F_v\,(J) \right| hc/kT\} \qquad (1)$$

where $c_{iso} = (a^i)^2\, b_v^2\, k_{\tilde{\nu}}$

and the symbols have their usual meaning[20].

Under the experimental conditions used here the individual rotational lines in each Q-branch are not resolved and the observed spectrum consists of unresolved Q-branch profiles for the vibrational transitions $1 \leftarrow 0$, $2 \leftarrow 1$, $3 \leftarrow 2$ etc. The relative intensities of the Q-branch profiles are temperature-dependent, with the intensities of the transitions originating from higher vibrational levels increasing relatively as the temperature increases.

Since all the molecular parameters in eqn. (1) are known for nitrogen the temperature that best reproduces the experimentally determined intensity profiles may be determined using an iterative computer-fitting program.

This program uses a triangular slit function with the FWHM matched to the experimental spectral slit-width of 5.3 cm^{-1} and minimises the least-squares deviations between experimental and calculated data points to give a best-fit temperature. All the information held in the 256 channels of computer memory on the micro-computer were transferred to the main-frame computer for this analysis.

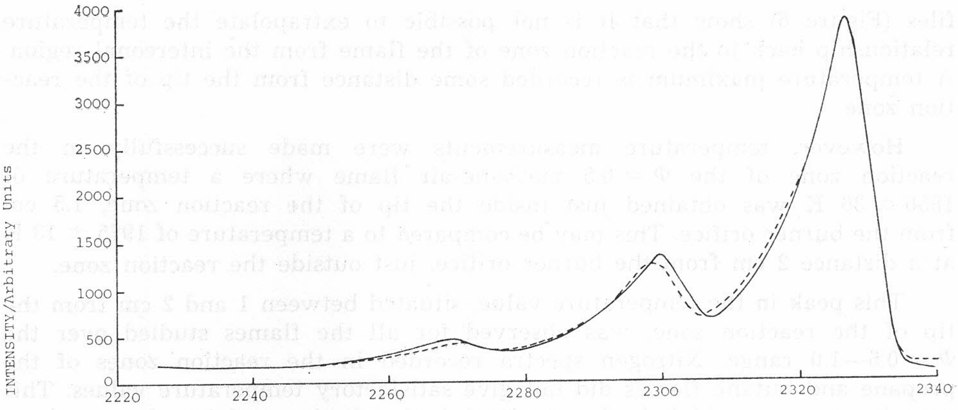

Figure 1. Unresolved Stokes Raman Q-branches, $\Delta\tilde{\nu} = 2220—2340$ cm^{-1}, for nitrogen in a methane-air flame, $\Phi = 0.5$, axial distance 5 cm above the burner orifice, radial distance 0 mm from burner axis. Observed spectrum ———; computer fitted spectrum - - - -. Calculated temperature $T = 1571 \pm 9$ K. Observed spectra collected in 256 channels.

The iterative computer-fitting program was written in FORTRAN 77 for use on a Control Data Corporation CYBER 170—172 computer system. The relevant molecular constants, experimental parameters and data file were supplied as input; changes in the spectral baseline and wavenumber calibration over extended periods could be accounted for within the program. An estimate of the temperature was provided in the input information. In practice, the computer program converged quickly to the best-fit temperature and on no occasion was it necessary for more than ten iterations to be performed before a final results was given. The program was not known to fail, regardless of how poor were the estimates of temperature.

An example of a calculated best-fit spectrum profile matched with observed spectral data is provided in Figure 1 for the propane-air system ($\Phi = 0.7$). A best fit of a given spectrum can usually be achieved to ± 1 K. Temperatures quoted in the form $T \pm \Delta$ K represent the mean temperatures, T, of 10—25 experiments with a standard deviation of $\pm \Delta$. The temperature is of course a time-averaged value over the period of measurement at that point in the flame.

RESULTS AND DISCUSSION

Figures 2—7 show some of the spectra recorded in the three fuel-air flames of interest and some corresponding temperature profiles plotted for each series of spectra. Data collected from both axial and radial scans of the flames are presented as examples of the results obtained. The temperature profiles, T versus x, where x is the axial or radial position of the laser focus in the flame, are plotted using the average temperatures obtained from three measurements at each point. The error bars mark the standard deviations obtained from the fitting of the calculated data with the experimental data. From these profiles the temperature gradients dT/dx can be evaluated.

The spectra obtained from the axial scans of each flame (Figures 2, 3 and 4) illustrate the increase in the noise level of the spectra as the flame is probed closer to the reaction zone. This is also shown in the axial temperature profiles, where a larger standard deviation in the temperature measurement is obtained from the noisier spectra. These axial temperature profiles (Figure 6) show that it is not possible to extrapolate the temperature relationship back to the reaction zone of the flame from the interconal region. A temperature maximum is recorded some distance from the tip of the reaction zone.

However, temperature measurements were made successfully in the reaction zone of the $\Phi = 0.5$ methane-air flame where a temperature of 1856 ± 36 K was obtained just inside the tip of the reaction zone, 1.5 cm from the burner orifice. This may be compared to a temperature of 1975 ± 13 K at a distance 2 cm from the burner orifice, just outside the reaction zone.

This peak in the temperature value, situated between 1 and 2 cm from the tip of the reaction zone, was observed for all the flames studied over the $\Phi = 0.5$—1.0 range. Nitrogen spectra recorded in the reaction zones of the propane and butane flames did not give satisfactory temperature values. This was due to a very high background level of radiation and interference from other reacting species. The butane-air flame proved to be the most difficult to study because of its luminosity and the results of 16 temperature measurements made at $\Phi = 0.5$ in this flame 4 cm from the burner orifice showed

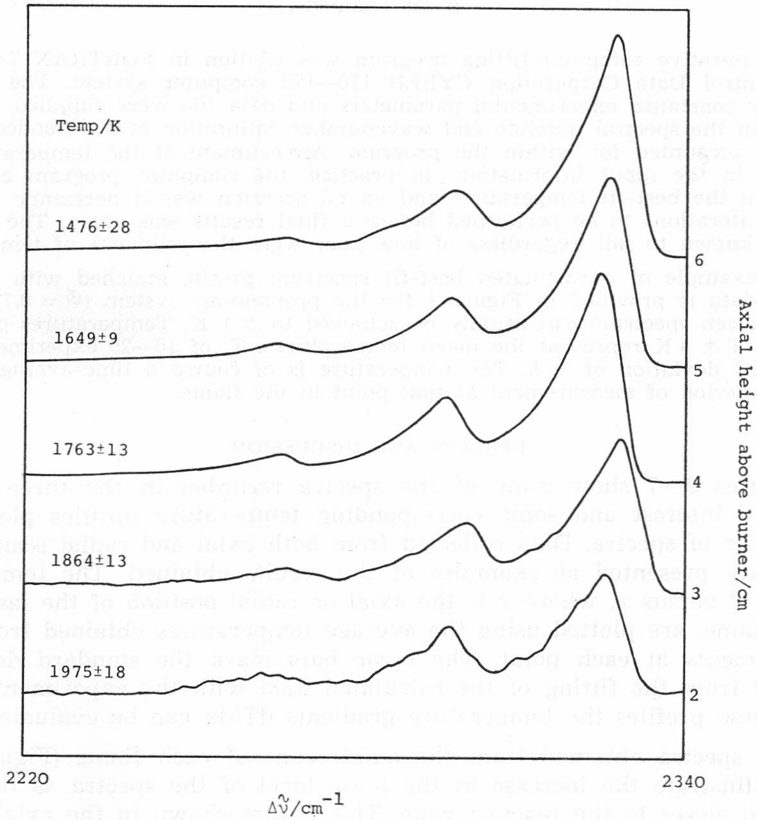

Figure 2. Stokes Raman spectra of nitrogen in methane-air flame, $\Phi = 0.5$, axial distance 2—6 cm above burner orifice. Radial distance 0 mm from burner axis.

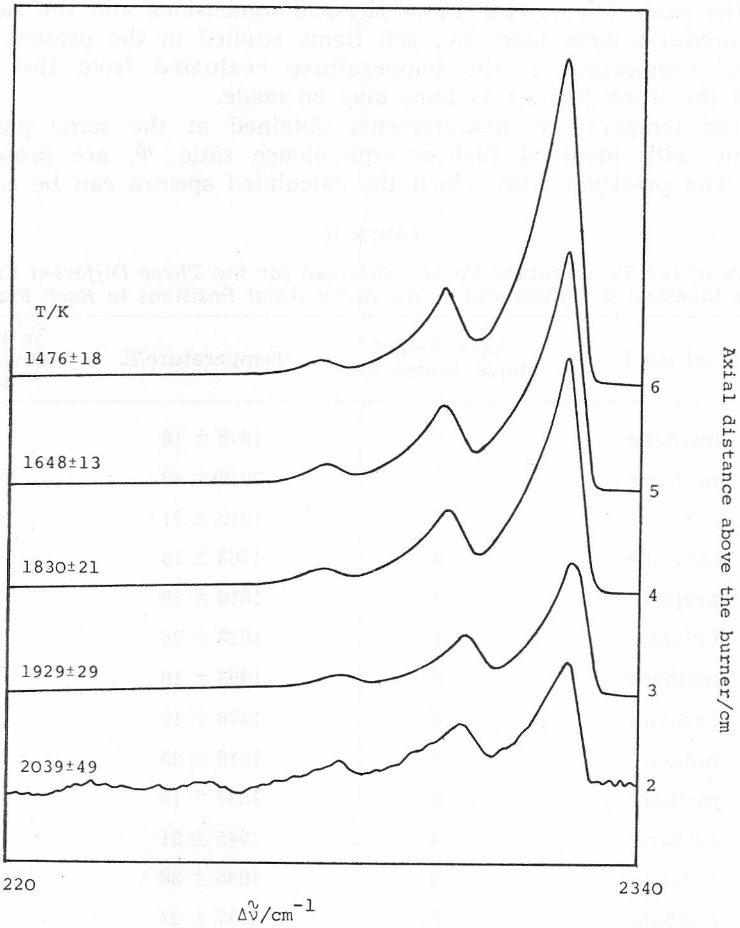

Figure 3. Stokes Raman spectra of nitrogen in propane-air flame, $\Phi = 0.5$, axial distances 2—6 cm above burner orifice. Radial distance 0 mm from burner axis.

a mean temperature of 1823 ± 26 K, this standard deviation of ± 1.4% being the largest observed in the systems studied. The temperatures obtained at the same point in the three flames, namely an axial distance of 4 cm above the burner orifice, are given in Table I.

TABLE I

Comparison of the Temperature Values Obtained for the Three Different Fuels at an Axial Height of 4 cm in Each Flame

Φ	Fuel used	Temperature/K	% standard deviation in the temperature
0.5	methane	1763 ± 13	0.7
0.5	propane	1816 ± 18	1.0
0.5	butane	1823 ± 26	1.4

Because the same burner, the same physical dimensions and the same analytical procedures were used for each flame studied in the present work, a meaningful comparison of the temperatures evaluated from the recorded spectra of the three fuel-air systems may be made.

Selected temperature measurements obtained at the same position in each flame with identical fuel-air equivalence ratio, Φ, are presented in Table II. The precision with which the calculated spectra can be computer-fitted to the experimental spectra is consistently higher in the methane-air flames. The precision in the fitting procedure generally decreases linearly with the carbon number of the fuel used. The average % standard deviations in the temperature measurements for each flame for $\Phi = 0.5 \rightarrow 0.7$ are 1.1, 1.6 and 2.3% for methane-air, propane-air and butane-air, respectively.

TABLE II

Comparison of the Temperature Values Obtained for the Three Different Fuels Used with Identical Φ Values and at the Same Axial Positions in Each Flame

Φ	Fuel used	Axial height above burner/cm	Temperature/K	% standard deviation in temp.
0.5	methane	2	1975 ± 18	0.9
0.5	propane	2	2039 ± 49	2.4
0.5	butane	2	1912 ± 71	3.7
0.5	methane	4	1763 ± 13	0.7
0.5	propane	4	1816 ± 18	1.0
0.5	butane	4	1823 ± 26	1.4
0.5	methane	6	1493 ± 19	1.3
0.47	propane	6	1476 ± 18	1.2
0.5	butane	6	1519 ± 25	1.6
0.6	methane	4	1837 ± 18	1.0
0.6	propane	4	1945 ± 31	1.6
0.6	butane	4	1965 ± 38	1.9
0.7	methane	5	1757 ± 23	1.3
0.7	propane	5	1810 ± 37	2.0
0.7	butane	5	1847 ± 67	3.6
0.7	methane	6	1524 ± 18	1.2
0.7	propane	6	1684 ± 24	1.4
0.7	butane	6	1775 ± 32	1.8

The temperatures obtained from the three flames are not significantly different. For the flames generated in the experiments reported the air flow rate, and consequently the O_2 flow rate, was held constant at 758 $cm^3\ min^{-1}$

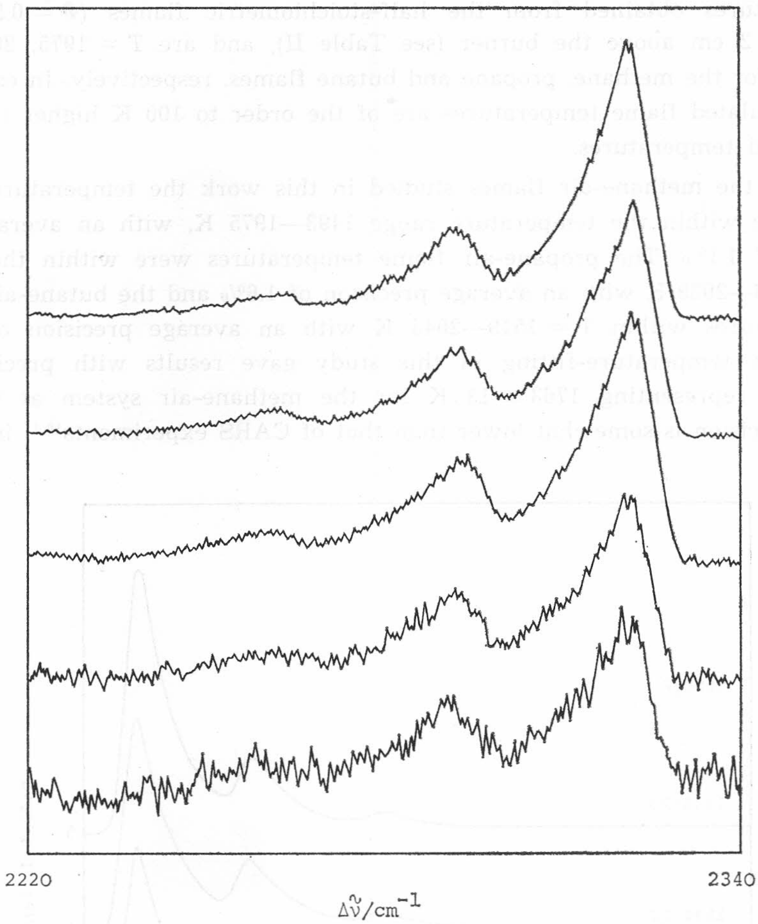

Figure 4. Stokes Raman spectra of nitrogen in butane-air flame, $\Phi = 0.5$. Axial distances 2.6 cm above burner orifice. Radial distance 0 mm from burner axis.

and the fuel flow rate vas varied to produce the flame of a desired Φ value. The fuel flow rates used to generate flames with $\Phi = 0.5$ for methane, propane and butane were 190, 76 and 58 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, respectively. Although the temperatures recorded in each flame are similar, the quantity of fuel required to generate a flame of this temperature and physical size is considerably less for butane than for methane because of the stoichiometry of the combustion reactions.

The maximum flame temperature attainable in the case of methane, propane and butane were calculated to be 2105, 2124 and 2122 K, respectively. In these calculations the combustion process for 1 mole of fuel in air has been assumed to be adiabatic. These calculated maximum temperatures can be compared with the hottest measured flame temperatures, which are the temperatures obtained from the half-stoichiometric flames ($\Phi = 0.5$) at a position 2 cm above the burner (see Table II), and are $T = 1975$, 2039 and 2043 K for the methane, propane and butane flames, respectively. In each case the calculated flame temperatures are of the order to 100 K higher than the measured temperatures.

For the methane-air flames studied in this work the temperatures measured lie within the temperature range 1493—1975 K, with an average precision of 1.1%. The propane-air flame temperatures were within the range $T = 1476$—2039 K with an average precision of 1.6% and the butane-air flame temperatures within $T = 1519$—2043 K with an average precision of 2.3%. The best temperature-fitting in this study gave results with precision of ± 0.7%, representing 1763 ± 13 K for the methane-air system at $\Phi = 0.5$. This precision is somewhat lower than that of CARS experiments[10,17] in which

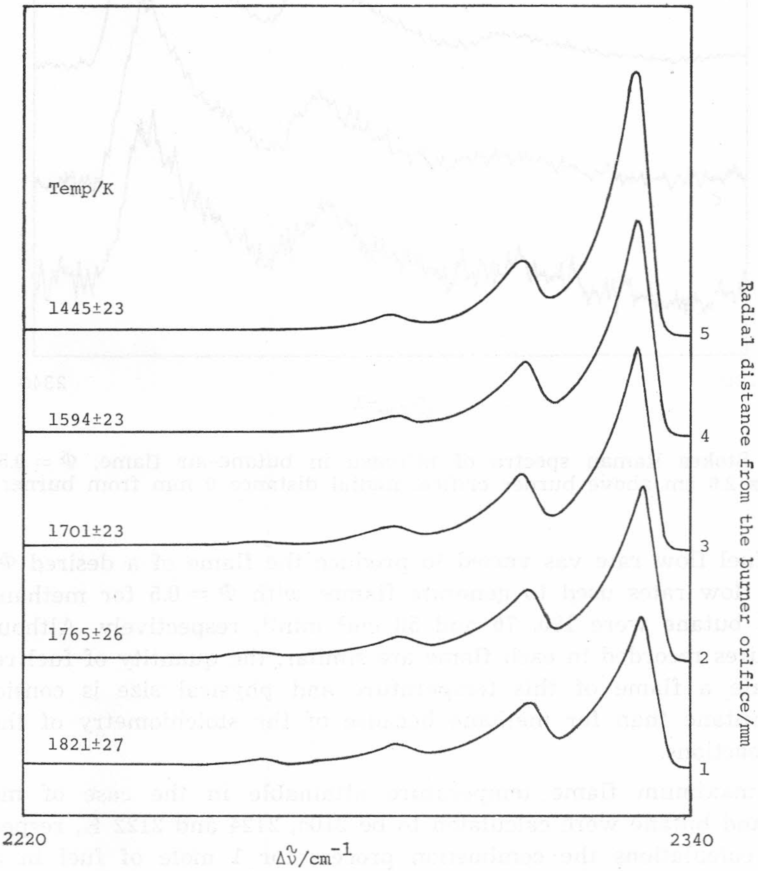

Figure 5. Stokes Raman spectra of nitrogen in propane-air flame, $\Phi = 0.5$. Radial distances 1—5 cm from burner axis at axial distance of 4 cm above burner orifice.

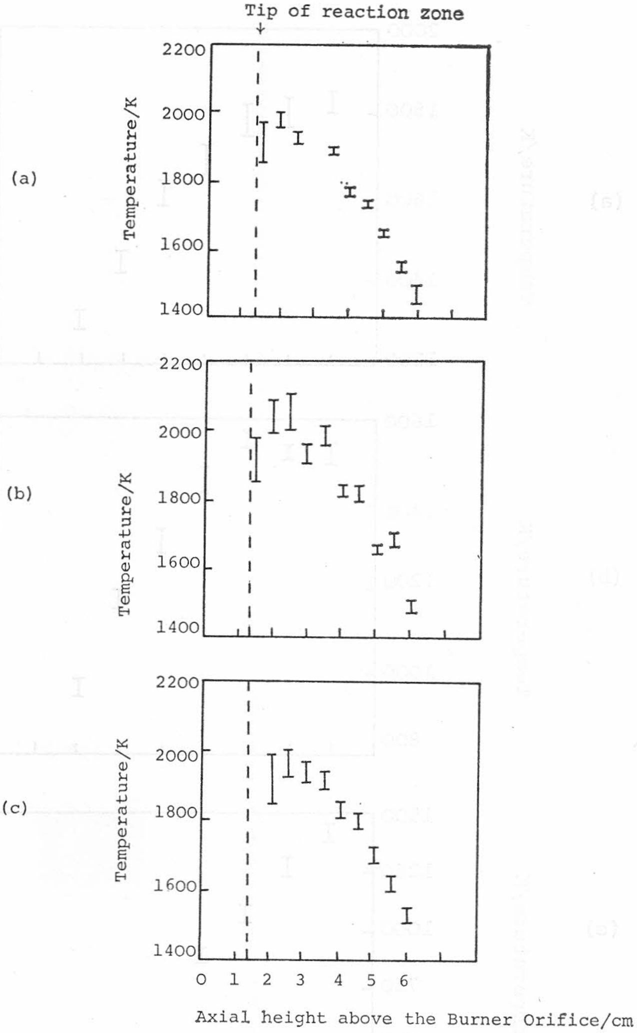

Figure 6. Axial temperature profiles of (a) methane-air, (b) propane-air, (c) butane-air flames, all $\Phi = 0.5$, for radial distance of 0 mm from the burner axis.

a best-fit temperature of 2104 ± 9 K (0.4%) for a pre-mixed methane-air flame was obtained.

The method of temperature measurement described here has good precision but is limited to flames which are stable over many minutes and which are non-luminous. The use of multichannel detection would reduce the period of measurement to the order of seconds. Then linear Raman spectroscopy could be used effectively for laboratory studies of selected systems, so avoiding the substantially higher cost of CARS equipment. However, in hostile environments and where high time resolution is important it cannot replace CARS.

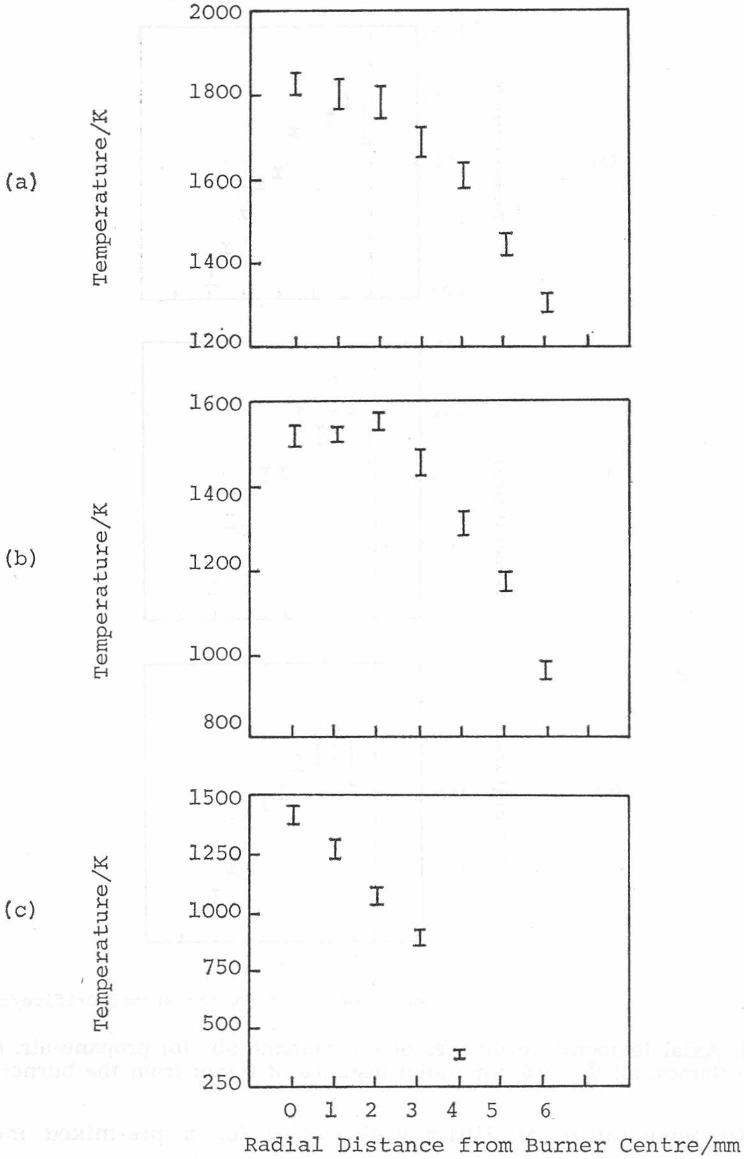

Figure 7. Radial temperature profiles in a butane-air flame, $\Phi = 0.5$, at axial heights of (a) 4 cm, (b) 6 cm, (c) 8 cm above the burner orifice.

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SAŽETAK

Određivanje temperature plamenova metan-zrak, propan-zrak i butan-zrak primjenom Ramanovih spektara Q-grane dušika

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Eksperimentalno su mjereni nerazlučeni profili Q-grana u Ramanovim spektrima dušika u laminarnim plamenovima metan-zrak, propan-zrak i butan-zrak, s osloncem na stehiometrijski ekvivalentan odnos gorivo-zrak, te korišteni za određivanje temperature plamena s točnošću od oko 1% primjenom iterativnog računskog postupka koji prilagođava proračunane spektre dušika eksperimentalnima. Prikazani su aksijalni i radijalni temperaturni profili, a rezultati su uspoređeni s proračunanima adijabatskim temperaturama plamena.