LASER RAMAN PROBE FOR FLAME TEMPERATURE

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LASER RAMAN PROBE FOR FLAME TEMPERATURE

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Experimental spectra of Raman Scattering Stokes fundamental vibrational Q-branches for nitrogen and hydrogen in hydrogen-air flames have been fit to theoretically-calculated profiles in order to determine temperature. The temperature measured from a least square fit of the full nitrogen profile agreed to within about 1.5% of the value calculated from the ratio of the peak intensity of the first upper state band (i.e., "hot" band) to that of the ground state band. Agreement with the temperature estimated from fine-wire thermocouple measurements was approximately 2%. Additional theoretical profile calculations are given from nitrogen and hydrogen over the wide range of temperatures.
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LASER Raman Probe for Flame Temperature

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Introduction

This work is directed toward the measurement of vibrational Raman scattering signatures for flame gases, with a primary view toward temperature measurements and a concomitant goal of identification and measurement of minor flame species. The development of an optical probe for these purposes is highly desirable, since advanced combustion systems are utilizing pressures and temperatures such that physical probes cannot survive. The use of a Raman scattering probe, in particular, offers a variety of advantages over other optical probes, along with some limitations which will be explored during the course of this work.

During this project reporting period, experimental effort has been focussed mainly on: (1) the observation and fitting of Raman Stokes vibrational Q-branch profiles for N₂ and H₂ obtained through
use of $N_2$-air flames produced on porous plug burners, (2) exploration of the accuracy of temperature measurement for $N_2$ through extended thermocouple calibrations and computer data-fitting techniques, and (3) construction and preliminary use of apparatus designed for use in these and other phases of this research project.

The theoretical effort during this project reporting period has been concentrated upon analytical calculations of Raman Stokes vibrational Q-branch profiles, suitably convoluted by experimentally-determined monochromator slit functions or interference filter band-passes. The main effort has involved analytical procedures necessary to determine the temperature, and has included both least-square data fitting of entire profiles as well as intensity ratios of suitably chosen spectral regions.
I. Experimental Equipment

The basic double monochromator experimental apparatus has been described previously.¹ (Ref. 1 is included here as Appendix 1.) New additions have been made to the combustion, spectroscopic, temperature-measurement and computer data handling capabilities in connection with several parallel programs in our laboratory. Those which pertain directly to the present research effort are described next in outline fashion:

(1) A horizontal hydrogen-oxygen burner system utilizing a Meker burner has been assembled, which will permit flames to be produced up to ca. 3030⁰K. This apparatus does not disturb the basic geometry of our double-monochromator system, since it permits use of a vertical laser beam passing through the flame in the same fashion as for our porous plug burner assembly used at ca. 1300-1700⁰K. The high-temperature burner is designed for production of "minor" flame species of high technological interest, such as OH. Preliminary design studies have also been carried out for auxiliary optics for utilization with a vertically burning flame. In this configuration, a line image (i.e., the scattering zone in the flame) must be rotated through 90 degrees. Design studies include both use of two additional mirrors and use of a Dove prism.

(2) Accurate flow metering techniques have been installed for the production of reproducible and clearly-defined flame conditions. The flows are now monitored and made steady by critical flow orifices and regulators, use being made of precision high-pressure gauges for accurate control of the flow rates. The critical flow orifices have been calibrated in our laboratory through use of basic volume-displacement techniques.
Fine wire thermocouples have been made in our laboratory for independent measurements of the flame temperature by a standard method. These thermocouples were made of 0.0005 inch diameter wires of Pt - Pt 10% Rh, coated with quartz to prevent catalytic heating. The thermocouples were moved throughout the flame with an accurate vernier manipulator using, as a reference position locator, a finely-machined metal cone which could be placed reproducibly on the burner head. When the burner assembly was then placed in the test position in front of the spectrometer, the burner could be accurately located in this same reference position by placing it so that the laser beam just touched the cone tip. (By observing slight attenuation of the laser beam with a power meter at the position of the laser dump, this positioning could be accomplished with high sensitivity.)

In principle, the thermocouple-measurement position and laser Raman scattering position could be made coincident by imaging the laser beam on the thermocouple junction. However, it is experimentally difficult to accomplish this. In addition, the thermocouples are relatively fragile, and it was therefore found to be advisable to calibrate the flame before embarking on the scattering measurements.

Additional temperature measurements have been made with a commercially-available 0.001 inch diameter Pt - Pt 10% Rh thermocouple with a bead-welded end, stretched out to the same linear geometry as was used for the 0.0005 inch diameter thermocouples described above. (See Fig. 1 for schematics of these two types of thermocouples.) This thermocouple was not quartz-clad, but had longer leads. The basic idea was to test the sensitivity of thermocouple measurement of temperature to thermocouple geometry, without embarking upon a major
Fig. 1 Schematics of thermocouples used for flame temperature calibrations. (The flame temperatures quoted are from a study in which thermocouples were compared, and do not correspond to the exact conditions for which the Raman scattering data and subsequent thermocouple temperature measurements were made.)
diversion of effort. The result was that a modest but not very signifi-
cant difference existed. The smaller thermocouple gave an uncorrected
temperature of 1705°K in a carefully controlled stoichiometric hydrogen-
air flame, while the larger gave 1718°K. These values are the average
of many measurements with only a small variation between measurements.
Since the correction for radiative losses (the largest correction here)
to be applied to thermocouple-measured temperatures is ca. 4 times
larger than this difference of values, the difference is not believed
to be highly significant.

(4) Data logging via paper tape for intensity and wavelength
has been installed in the double monochromator system. This apparatus
permits data to be accumulated in a far more accurate and convenient
fashion, making full use of our computer facilities. In Fig. 2 is
shown the electronic detection schematic for this apparatus. The
wavelength data is obtained through use of an optical incremental
encoder installed on the double monochromator. This system, now
operational, is currently being improved by location of a new optical
encoder element directly on the wavelength screw (rather than in a
more remote mechanical location, as is presently the case). The en-
coding of accurate wavelength data is considered important because use
of an inaccurate (non-linear, etc.) wavelength axis in fitting experi-
mental Raman vibrational Q-branch profiles to theoretical shapes
results in distortion which, in turn, lead to inaccurate computer fits
and therefore inaccurate temperatures.

(5) An interference filter-test cell apparatus has been constructed
which is capable of operation with a porous plug burner. A photograph
of the apparatus appears as Fig. 3, while a schematic is shown in Fig. 4.
Fig. 2 Electronic detection apparatus for double monochromator, including photon counting equipment, digital intensity and wavelength data encoding equipment, and computer processing equipment. Photons (labeled "hv") are shown leaving the exit slits of the double monochromator.
Fig. 4  Schematic of interference filter-test cell apparatus designed for photon-counting operation.
Preliminary operation of this test cell with several hydrogen-oxygen flames has identified areas of needed additional development work. Particular attention is now being given to cooling of the interference filters, since the filter passbands shift with the temperature, and do not return to their initial positions when the original temperature is restored.

II. Experimental Conditions

All experiments discussed here utilized the double monochromator and horizontally-burning hydrogen-air flames on a 2.5 cm-diameter water-cooled porous plug burner which was placed 2.0 cm away from another water-cooled porous plug connected to a vacuum line. A continuous wave argon ion laser source of about 1 watt at the flame position at 480 nm was used for all the results reported here. The temperatures of the flames were measured as a function of position by means of the fine thermocouples described in the previous section.

Two different flames were studied. First, for nitrogen data, a steady stoichiometric hydrogen-air flame was utilized (37.5 cc/sec. H₂ and 88.8 cc/sec. air) for which 65% of the product gases was nitrogen. The flame was found to be about 1575 K at its center point (i.e., halfway between the burner head and the vacuum plug), including a rough 50 K correction for thermocouple radiative losses. Since the image of the monochromator entrance slits at the flame scattering position was about 5 mm high, an estimate was made of the temperature variation along this zone. This was found to be about 16 K. The reproducibility of the thermocouple data was about ± 1 K.
Second, for hydrogen data, a less steady fuel-rich (four times stoichiometric) hydrogen-air flame was used (79.3 cc/sec. H₂ and 47.0 cc/sec. air) for which about 51% of the product gases was hydrogen. This flame was found to be about 1390 K at its center point, including a rough 40 K correction for radiative losses. Here, the variation of temperature with position along the slit image was much more severe, being roughly 110 K over a 5 mm vertical zone. Furthermore, the reproducibility was significantly poorer, i.e., roughly ± 30 K. This flame, colored red from the emission of water vapor vibration-rotation bands, was subject to significantly more diffusion by the ambient atmosphere than the preceding flame, which undoubtedly contributed to its less reproducible characteristics. It had, however, the virtue of a high hydrogen content.

III. Theoretical Predictions of Band Profiles

For the diatomic molecules considered in these experiments, Eq. (3) of Ref. 1 (see Appendix 1) can be used for the calculation of the Stokes Q-branch fundamental series (v'v+1v) profiles. This intensity relation neglects the small depolarized contribution for our cases. The profiles calculated in Ref. 1 in this fashion were used to fit experimental profiles in order to determine the scattering-gas temperature. Therefore, all calculated profiles were normalized to the experimental curve peaks. Such normalized profiles are also used here in computer fits for temperature determination (see Fig. 13), but for other purposes, it is desired to calculate profile for a given molecule at various temperatures while maintaining the spectral intensity differences at these temperatures.
(i.e., not normalizing each profile at the peak intensity). This is the case, for example, if it is desired to calculate the relative intensities at different temperatures obtained through use of a monochromator or filter designed to isolate a spectral portion of the Q-branch. We point out here that Eq. (3) of Ref. 1 can be used for these calculations if the vibrational partition function $Q_{vib}$ given in Ref. 1 following Eq. (3),

$$Q_{vib} \propto [1 - \exp(-hc\omega_e/kT)]^{-1},$$

is multiplied by the factor $\exp[-(hc/kT)G(O,O)]$, where $G(O,O)$ is the zero-point energy. Here:

$$G(O,O) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_x + \frac{1}{8}\omega_y,$$

where $\omega_e$, $\omega_x$, and $\omega_y$ are vibrational constants defined by Eq. (1) of Ref. 1. The exponential factor compensates for the fact that the term value $G(v,J)$ defined by Eq. (1) of Ref. 1 relates to the energy above zero rather than above the zero-point energy.

Furthermore, substitution of $\omega_o$ for $\omega_e$ in Eq. (1) for $Q_{vib}$, where

$$\omega_o \approx \omega_e - \omega_x + \frac{3}{4}\omega_y,$$

results in a slightly more accurate calculation of $Q_{vib}$. Here, $\omega_o$ is the coefficient of the linear v term in the term value expression

$$G_o(v) = \omega_o v - \text{constant} x(v^2) + ...$$

Finally, if comparisons of Q-branch intensities are to be made between different molecules, account must be taken of the absolute
value of the nuclear spin statistical weight $g_I$. This may be accomplished by substitution of $g_I$ for the relative factor $n$ in Eq. (3) of Ref. 1, and, for $\Sigma$ states of homonuclear molecules, multiplication of the value of $Q_{\text{rot}} \propto kT, 2hcB_0$ given in Ref. 1 following Eq. (3), by the factor $(2I+1)^2$. Here, $I$ is the nuclear spin quantum number.

In analogy with the previous comment on $Q_{\text{vib}}$, substitution of $B_0$ for $B_e$ in the relation for $Q_{\text{rot}}$ results in a slightly more accurate calculation of $Q_{\text{rot}}$. Here,

$$B_0 \propto B_e - a_e/2$$

where $a_e$ is the coefficient of the vibration-rotation interaction term in the term value $G(v,J)$ given in Eq. (1) of Ref. 1.

In Fig. 5(A) are shown the calculated nitrogen rotational lines of the vibrational Q-branch at 1000 K, different symbols denoting the various fundamental bands. The nitrogen spectrum has alternately "strong" and "weak" lines because of nuclear spin degeneracy, but only the "strong" lines are shown here for clarity. In Fig. 5(B) is shown the spectrometer slit-convoluted intensity appropriate for the instrument used in our work, viz., a triangular slit function of full width at half maximum (FWHM) $\Delta = 1.63\lambda$ corresponding to 300 nm entrance and exit slits on a Spex 1400-1 double spectrometer. The same type of calculations for 2000 K and 3000 K are shown in Figs. 6 and 7, respectively.

Use of the type of data shown in Figs. 5-7 permits estimation of appropriate spectral regions for measuring the various rotational and vibrational excitation temperatures possible. In general, vibrational temperatures are proportional to the integral of intensity for particular bands (i.e., the ground state band or any specific upper state.
Fig. 5 Calculated Stokes Q-branch fundamental intensity at 1000°K for nitrogen. (A) Alternate "strong" line intensities. The square data points correspond to the ground state band and the circular points to the first upper state band. (B) Triangular slit function-convoluted profile, where $\Delta$ is the spectral slit width (FWHM).
Fig. 6 Calculated Stokes Q-branch fundamental intensity at 2000°K for nitrogen. (A) Alternate "strong" line intensities. The square data points correspond to the ground state band, the circular points to the first upper state band, the open triangular points to the second upper state band, etc. (B) Triangular slit function convoluted profile, where $\Delta$ is the spectral slit width (FWHM).
Fig. 7 Calculated Stokes Q-branch fundamental intensity at 3000°K for nitrogen. (A) Alternate "strong" line intensities. The square data points correspond to the ground state band, the circular points to the first upper state band, the open triangular points to the second upper state band, etc. (B) Triangular slit function convoluted profile, where $\Delta$ is the spectral slit width (FWHM)
band), while rotational temperatures are proportional to the profile on the short wavelength side of each band via the influence of the vibration-rotation interaction. Thus, in principle, it is possible to determine vibrational excitation temperatures for any pair of vibrational levels, and rotational excitation temperatures associated with any vibrational level.

For general comparative purposes, the nitrogen profile has been calculated from 300°K to 3500°K in Fig. 8 for $A = 1.58$. Here, the relatively broad spectral width at elevated temperatures becomes quite apparent.

The profiles for hydrogen are very different from those for nitrogen, since the individual vibration-rotation lines of the Q-branch for light molecules are spread far apart because of their very large vibration-rotation interaction constant, $a_e$. (For hydrogen, $a_e$ is over 6 times larger than the value for nitrogen.) In Fig. 9 are shown calculated shapes for hydrogen from 300°K to 1500°K, while in Fig. 10 are shown the profiles for 1900°K to 3500°K. We note that the first vibration-rotation line of the first upper state band in hydrogen does not appear for a longer spectral interval [starting from the (0,0) position, where the parenthetical notation corresponds to the lower level quantum numbers $(v,J)$] than that corresponding to the entire wavelength scale of all the nitrogen data plotted in Fig. 8.

IV. Experimental Results for Nitrogen

The profile of nitrogen observed from the stoichiometric flame at a thermocouple-measured temperature of 1575°K (1525°K indicated temperature, plus an estimated 50°K correction for radiative losses) is shown in Fig. 11
Fig. 8 Calculated Stokes Q-branch fundamental intensities for nitrogen from 300K to 3500K.
Fig. 9 Calculated Stokes Q-branch fundamental intensities for hydrogen from 300°K to 1500°K. The vertical lines along the wavelength axis indicate the positions of the various (ν,J) vibration-rotation lines, where the parenthetic notation corresponds to the lower level quantum numbers.
Fig. 10 Calculated Stokes Q-branch fundamental intensities for hydrogen from 1900°K to 3500°K. The vertical lines along the wavelength axis indicate the positions of the various (v,J) vibration-rotation lines, where the parenthetic notation corresponds to the lower level quantum numbers.
Fig. 11 Analog x-y recorder trace of Stokes vibrational Q-branch for nitrogen.
as recorded by an analog x-y recorder. The same data as recorded by paper tape data logging appears in Fig. 12. Here, the number of counts was recorded every ten seconds (i.e., every 0.02 nm for the spectrometer scan speed used).

In order to theoretically fit the experimental profile and thereby determine the nitrogen temperature, the experimental data wavelength axis was first made coincident with the proper theoretical wavelength axis by manually overlaying the experimental data on a normalized (i.e., at the ground state band peak) set of theoretical profiles. (See Fig. 13) These profiles all have very similar long-wavelength edges, determined over this temperature range almost entirely by the monochromator slit function shape. This long-wavelength edge was therefore useful in determining the proper absolute wavelength values for the experimental data. In future work, it is contemplated to perform this axis adjustment (required for slight backlash in the monochromator scanning mechanism) automatically through use of a computer-fit of the long-wavelength edge utilizing an initially assumed approximate temperature.

The next step in the determination of temperature involved a calculation based upon the ratio of intensities recorded by the monochromator in the vicinity of the peaks of the first upper state band and the ground state band. (See Fig. 14) Each of these bandpasses was 0.18 nm wide, and contained ten data points. The theoretical ratio shown in Fig. 14 was stored as a data file in the computer, and the computer-determined peak ratio for the experimental data could then be compared to this data file, resulting in a determination of temperature. The theoretical ratio of peak bandpass intensities is

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Fig. 12 Stokes vibrational Q-branch for nitrogen recorded by data logging in 0.02 nm intervals corresponding to the same conditions as for Fig. 11.
Fig. 13 Theoretically-calculated Stokes vibrational Q-branches from 1300°K to 1700°K, with peak ground state band intensities all normalized to unity. The sensitivity of these profiles to temperature for experimental profile-fitting procedures is illustrated by this set of curves.
Fig. 14 Intensity ratio as a function of temperature for 0.18 nm rectangular bandpasses in the spectral vicinity of the first upper state band and ground state band for the nitrogen Stokes vibrational Q-branch.
also shown in Fig. 15 over a smaller temperature range applicable to porous plug burner experiments. This ratio is almost exactly linear over this range of temperature. For the flame studied here, the temperature determined by this procedure was 1546°K.

The final step in temperature measurement involved a least-square computer curve-fitting treatment of the experimental data. The initial assumed temperature for this procedure was that determined from the band peak ratio method just described. The minimum least-square deviation was then searched for by the computer as a function of temperature, and the temperature corresponding to this minimum deviation determined thereby to the nearest 1°K.

This method of temperature determination has a basic shortcoming in that it is based upon use of raw monochromator data, to which the peak of each trial theoretical profile must be normalized. Thus, any noise "spike" of other random inaccuracy in the ground state band peak intensity can cause a substantial distortion of the curve fitting procedure by producing a "false" normalization, with subsequent vertical stretching or squeezing of the profile. This problem can be circumvented by the averaging of adjacent data points, which can be performed by the computer to produce a new "smoothed" experimental data file. A program has been written to accomplish this smoothing by averaging over any odd number of data points in an equally-weighted fashion. Thus, for a three-point data average at wavelength \( \lambda \), with \( \delta \) equal to the spectral interval between data points, the new intensity at \( \lambda \) corresponds to \((1/3)\) times the originally-encoded intensities at \( \lambda-\delta \), \( \lambda \), and \( \lambda+\delta \).
Fig. 15  Intensity ratio as a function of temperature for 0.18 nm rectangular bandpasses in the spectral vicinity of the first upper state band and ground state band for the nitrogen Stokes vibrational Q-branch. The intensity ratio over the temperature range shown here is almost exactly linear with temperature.
In turn, this method of data smoothing has a clear shortcoming in that it also distorts the overall profile in the vicinity of sharp, nonlinear changes of intensity. Thus, a compromise approach is dictated, in which data smoothing is accomplished over an optimized spectral interval. This has been done for the data shown in Fig. 12, for which three-point, five-point, and seven-point data averages were taken. In Fig. 16 is shown the three-point averaged data, while the five-point averaged data is shown in Fig. 17 along with a theoretically-calculated profile computed at $T = 1546^\circ K$ (the temperature determined by the peak ratio method described previously) and normalized to the peak of the data-averaged experimental curve.

In the table contained in Fig. 18 is shown the results of the least square computer fitting procedure for the raw monochromator data, and the three-point, five-point, and seven-point averaged data. The temperature corresponding to the minimum deviation [i.e., $T(\text{min})$, corresponding to the minimum value of $\Sigma(\text{deviations})$] for each treatment of the data increases here as the amount of data averaging increases. It is easily seen that as the data averaging is increased excessively, the spectral profile is "flattened out", resulting in an appearance closer to that corresponding to higher temperatures.

As a working criterion for determining the optimum amount of data averaging, the procedure chosen utilized the smallest "minimum value of $\Sigma(\text{deviations})". As may be seen in the table contained in Fig. 18, the smallest value occurred for the five-point data average and, accordingly, this was chosen as the appropriate treatment for the data. The graph shown in Fig. 18 illustrates the variation of $\Sigma(\text{deviations})$ with temperature for the five-point data average, and indicates resultant best fit at a value of $T(\text{min}) = 1538^\circ K$. 

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Fig. 16 Three-point data-averaged Stokes vibrational Q-branch profile for nitrogen, obtained from the raw data of Fig. 12
Fig. 17  Five-point data-averaged Stokes vibrational Q-branch profile for nitrogen, obtained from the raw data of Fig. 12. Also shown is a theoretically-calculated profile for 1546°C normalized to the experimental peak ground state band intensity.
\[ E = \sum (\text{deviations})^2_T - \sum (\text{deviations})^2_T \]

Table: Summary of temperatures \( T(\text{min.}) \) corresponding to the minimum value of \( \sum (\text{deviations}) \) for the least square profile-fitting procedure, computed for the raw monochromator data and for three cases of data averaging. Figure: Variation of \( \sum (\text{deviations}) \) as a function of temperature for the five-point data-averaged profile.
Summarizing our findings for the accurate determination of flame temperature for nitrogen:

1. Sensitivity for measurement by averaged band peak ratios is shown in Figs. 14 and 15.
2. Sensitivity for curve fitting is illustrated by the set of normalized curves shown in Fig. 13.
3. The temperature measured by the band peak ratio was 1546°C.
4. The temperature measured by the best (five-point) data-averaged computer profile fit was 1530°C.
5. The temperature indicated by the fine wire thermocouple was 1525°C plus an approximate 50°C radiative correction, for an estimated flame temperature of 1575°C.

Current agreement between the peak intensity ratio method and the curve fitting method is about ½%. It is intended to pursue these techniques to determine their limiting accuracies, with an emphasis on variations of the methods which produce good accuracy with a minimum of complexity in the data handling. Thus, the trend is toward utilizing the full profile fit as a "calibration" of the simple band ratio method. This latter method can be made more accurate by utilizing more than the presently-used two bandpasses.

The full profile-fitting method will retain its utility for investigations of non-thermal equilibrium signatures. It will be particularly useful when neither vibrational nor rotational equilibrium exists. In this case, a deconvolution of the Raman scattering profile results in a determination of the relative populations of the various vibrational and rotational levels.
It is stressed here that Raman scattering signatures are direct measures of the relative populations of the molecular internal modes, and, for equilibrium situations, these relative populations correspond to the fundamental definition of temperature. Thus, it is contemplated that this form of temperature diagnostics has the potential for becoming the most fundamentally accurate scheme for non-perturbing, three-dimensional measurements.

V. Experimental Results for Hydrogen

The nitrogen data discussed in Section IV were taken with a view toward high-accuracy temperature diagnostics. The hydrogen data discussed in this section were taken in order to investigate the different type of Raman vibrational signature produced by a very light molecule, and were not intended for accurate temperature measurements.

The profile of hydrogen obtained from a four-times-stoichiometric hydrogen-air flame at a thermocouple-measured temperature of about 1350\(^\circ\)K (corrected roughly for radiative losses) is shown in Fig. 19 as observed through use of an analog x-y recorder. The first four rotational lines of the Stokes vibrational Q-branch are identified. (For purposes of comparison, see Fig. 9 for a theoretically-calculated curve of the entire Q-branch at 1500\(^\circ\)K.) In Fig. 20 is shown the same data as obtained from the paper tape data logger, where the trace shown as the solid curve contains the Raman scattering data, and the dashed curve is a subsequently-run emission spectrum of this luminous flame. The emission spectrum has been subtracted from the emission-plus-scattering spectrum in Fig. 21, and a theoretically-calculated (dashed) curve added for hydrogen at 1400\(^\circ\)K. Keeping the J = 3
Fig. 19 Analog x-y recorder trace of first few rotational lines of Stokes vibrational $Q$-branch for hydrogen.
Fig. 20 Experimental Stokes Q-branch fundamental profile (solid curve) for hydrogen for four-times-stoichiometric hydrogen-air flame $\left(8H_2 + O_2 + 3.73 N_2 \right)$. The dashed curve is a subsequently-run emission spectrum for this slightly luminous flame. The thermocouple-measured temperature was approximately $1390^\circ K$, and the spectral slit width $\Delta = 1.62 \AA$. 
Fig. 21 Experimental Stokes Q-branch fundamental profile (solid curve) for hydrogen for the conditions of Fig. 20. Here, the emission spectrum (dashed curve of Fig. 20) has been subtracted from the scattering-plus-emission spectrum (solid curve of Fig. 20). A theoretically-calculated profile for hydrogen at 1400°K (dashed curve) has been added, and has been normalized to the experimental peak intensity for the J = 3 line. Keeping the peak intensities normalized for the J = 3 line, profiles were calculated at 1300°K and 1500°K. The corresponding peak intensities of the J = 0, 1, and 2 lines are indicated here by horizontal bars.
calculated peak intensity normalized to the experimental peak intensity, profiles were also calculated for other temperatures. The peak values for $J = 0, 1, \text{ and } 2$ at $1300^\circ\text{K}, 1400^\circ\text{K}, \text{ and } 1500^\circ\text{K}$ are indicated by the appropriate horizontal lines in this figure. The accuracy of temperature measurements for the hydrogen data shown here is not good for two main reasons: (1) the flame is somewhat unsteady and non-isothermal, and (2) ratios of the vibration-rotation line intensities shown here are not particularly sensitive to the temperature over this temperature range. Other ratios utilizing higher rotational lines are more sensitive for this range. However, the profile presented here is indicative of the type of data and the required treatment for temperature estimates utilizing light molecules. The relatively wide spectral intervals between vibration-rotation lines for these molecules suggests that, with proper choice of bandpass, interference filters could eventually be used for temperature determinations with greater ease than would be the case for heavier molecules.

VI. Conclusion

The vibrational Raman signatures for nitrogen and hydrogen have been studied for hydrogen-air flames produced on a water-cooled porous plug burner. Accurate determinations of temperature have been performed utilizing the nitrogen data from a band ratio method and from a total profile-fitting procedure. These determinations as well as various other theoretical predictions have made wide use of computer calculation techniques. The temperatures found from the Raman methods agreed with each other to within $\frac{1}{2}$ percent, and agreed with an independently measured temperature utilizing a fine
wire thermocouple (only roughly corrected for radiative losses) to within 2%.

The hydrogen signature has been fitted to theoretical predictions for low-lying rotational lines, and exhibits a spread-out structure which may be particularly useful for temperature diagnostics. Additional equipment has been assembled for improvements in the spectroscopic, combustion, temperature-measurement, and data acquisition and reduction aspects of the experimental program. These will be used in further study of laser Raman probes for combustion diagnostics.

Acknowledgments

The author is grateful to Dr. John Moore for thermocouple fabrication, to Mr. Harry Horton for his contributions to thermocouple temperature and gas flow measurements, and to Mr. Frank Haller for computer programming. Some of the preliminary material reported here was presented by M. Lapp at the Third International Conference on Raman Spectroscopy, Reims, France, 1972.

References


Appendix 1

Raman Scattering from Flames

M. Lapp, L.M. Goldman, and C.M. Penney

Science 175 1112 (1972)
Raman Scattering from Flames.
End view of a flame burning horizontally on a porous plug burner (2.5 centimeters in diameter). A focused laser beam is passing vertically through the flame for Raman scattering experiments. See page 1112. [S. W. Blanchard, Graphics Unit, General Electric Co., Corporate Research and Development, Schenectady, New York]
Raman Scattering from Flames

Abstract. Laser Raman scattering data for nitrogen, oxygen, and water vapor have been obtained from hydrogen-air and hydrogen-oxygen flames. The resulting ground-state and upper-state vibrational bands exhibit strong asymmetrical broadening. Experimental spectral profiles have been fitted theoretically to give a new measurement technique for the determination of rotational and vibrational excitation temperatures.

We report here observations of vibrational Raman scattering from flame gases. One motivation for these observations is that Raman scattering can provide spatially resolved measurements of the concentration and the rotational and vibrational excitation temperatures of flame constituents. This capability should prove to be of substantial use in the diagnosis of nonequilibrium as well as equilibrium phenomena.

The work presented here is focused upon the observation of temperature-dependent effects in the spectral distribution of the Stokes Q-branch vibrational scattering. These effects arise predominantly from the vibration-rotation interaction and from significant populations of excited vibrational levels. From these excited levels originate upper-state bands (1) which are usually shifted toward the blue region of the spectrum.

In Fig. 1 we show the types of fundamental vibrational Raman scattering events that may be observed in flames. Earlier Raman scattering experiments at elevated temperatures have dealt with laser heating of a vapor (2), with studies of species in ovens at temperatures up to 1000°C (3), and with a low-pressure electric discharge (4). We have been unable to find any earlier publications concerning Raman scattering in flames or in any systems at temperatures in excess of 1000°C.

Our initial observations were confined to Stokes bands arising from 4880-Å incident radiation from an argon ion laser (Coherent Radiation model 52B) operated for most data at 1.5 watts. The scattered light was analyzed by a double monochromator (Spex 1400-II) with 5000-Å blazed gratings. The detector was a cooled photomultiplier (RCA C31000E Quantacon) operated in the pulse-counting mode with dark current levels of about 15 counts per second for this work.

The overall experimental arrangement was designed to have the laser beam traveling along the direction of the entrance slits (that is, vertically) and focused at a position about 0.3 m from the entrance slit. The Raman-scattered radiation was collected by a multifiber lens with a focal length of 75 mm. The width of the laser beam in the scattering zone was about 100 μm, and the height from which the scattered radiation was accepted (as determined by the 1-cm slit height and the image magnification factor of 10) was about 5 mm. The monochromator entrance and exit slits were set to 300 μm, for which the spectrometer with the value calculated from the instrument dispersion curve. The (Rayleigh and Mie scattering) image of the laser beam at the entrance slits (as viewed by a periscope attachment behind the slits) showed no change when the flame was ignited.

The flames studied were produced on a water-cooled porous plug burner (diameter, 2.5 cm) (5) operated horizontally and burned into another water-cooled porous plug (of larger diameter) placed about 1.5 cm away which was, in turn, connected to a rough vacuum line. In this fashion, a stable horizontal flame at atmospheric pressure was produced which possessed the advantage of offering a scattering test zone of uniform conditions (that is, at a constant distance from the flat flame front) for a laser beam passing in the vertical direction. Scattering data for H2O and O2 were obtained from lean H2-O2 flames, whereas data for N2 was obtained from a lean H2-air flame. Because of the low luminosity of these flames in the spectral regions of interest, no increase in background was observed when the flames were ignited. Precise flow data were not taken, nor

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were accurate independent temperature measurements made, since the major goal of this portion of our flame Raman scattering investigation was the exploration of general temperature-sensitive features of scattered bands. The temperatures actually determined from the scattering data are reasonable values for the flames used.

Although vibrational temperatures have been determined from the Stokes/anti-Stokes ratios of vibrational scattering (2, 6), the same information is accessible from the Stokes scattering alone. Our initial attention to the latter is due in part to the greater sensitivity of our spectrometer and detector to the Stokes scattering. However, there is also a potential advantage to this approach which arises from the fact that temperature measurements from Stokes (or anti-Stokes) scattering alone involve a much smaller spectral range than with the corresponding measurements of Stokes/anti-Stokes ratios. Thus, in the former case it is easier to correct for the spectral variation of background, absorption, and spectrometer response.

The asymmetry of the vibrational bands is evident even at room temperature for the molecules considered here, and particularly so for H2O. In Fig. 2B the H2O vibrational ground-state band is shown for scattering from room temperature ambient H2O. The greatly increased broadening toward the blue region of the spectrum under flame conditions is shown in Fig. 2A. The strong asymmetry of the N2 and O2 vibrational bands under flame conditions can be seen in Figs. 3 and 4. This "blue asymmetry" is explained by the fact that all the ΔJ = 0 rotational lines corresponding to the Q-branch do not overlap each other exactly. There is a progressive shift to shorter wavelengths caused by the vibration-rotation interaction term of the energy levels for a molecule. To discuss the spectral shape and position of each band, we consider the term value G(v,J) for a real diatomic molecule (7), including contributions from harmonic and anharmonic oscillator terms, rigid and anharmonic rotation terms, and vibration-rotation interaction terms (8).

\[ G(v,J) = \frac{E(v,J)}{h \nu} = \omega_v(v + \frac{1}{2}) - \omega_x(v + \frac{1}{2})^2 - \omega_y(v + \frac{1}{2})^3 + \omega_z(v + \frac{1}{2})^4 + \cdots \]

Here \( E(v,J) \) is the energy of the level \( (v,J) \); \( h \) is Planck's constant; \( c \) is the speed of light; \( \nu \) is the wavenumber; \( \omega_v \) is the vibrational frequency; \( \omega_x, \omega_y, \omega_z \) are the anharmonic constants; and \( \omega_{v,J} \) is the ground-state rotational constant.

![Fig. 1 (left). Schematic of some molecular transitions which contribute to fundamental vibrational Raman scattering (Δν = ±1).](image)

![Fig. 2 (right). (A) The H2O Raman vibrational ground-state band for a lean H2O flame. The partial segment above the solid trace is a portion of another measurement shown to indicate the reproducibility of the gross features at positions (a) and (b). The latter is an upper-state band and is discussed at the end of this report. Although feature (a) approximately coincides with a weak Ar line at 5925 Å, experimental measurements failed to show sufficient scattering of this radiation to cause the observed signal. (B) The same H2O Raman band taken in the laboratory atmosphere (295°K, 8 torr). The dashed curve is the spectrometer slit function. These curves correspond to 300-μm entrance and exit slits, for which the slit width \( \Delta \) is 1.62 Å at this wavelength. The wavelength axes of these curves are indicated in a relative fashion only, since wavelength calibration lines were not included in the experiments and theoretical profiles have not yet been calculated. The wavelength \( \lambda_n \approx 5934.5 \) Å is slightly to the right of the peak of (B) (that is, at slightly longer wavelength). As an example of a case for which exact calculations are not complicated, the peak of the 295°K slit-convoluted profile for N\(_2\) is at a wavelength about 0.3 Å less than the corresponding value of \( \lambda_n \).]
speed of light: \( n_o = n_r = n_\alpha \) are vibrational constants such that \( n_{\alpha r} \leq n_r \); \( B_r \) and \( D_r \) are, respectively, the rotational constants for rigid and nonrigid rotation in the equilibrium internuclear position; and \( v_r \) and \( \beta_r \) (\( \alpha_r \), \( B_r \), and \( D_r \) represent vibration-rotation interactions.

The Raman shift for a fundamental vibrational band (that is, for \( \Delta \lambda = 0 \) and \( \Delta v = 1 \)) is, from Eq. 1:

\[
\Delta \nu(r + 1 - \nu, r + 1) = \nu_o - 2\omega_r(r + 1) + \omega_r(3r^2 + 6r + 13/4) - \alpha_JU + 1 - \beta_r(I + 1)^4 + \ldots \]

where the vibration-rotation interaction, corresponding to the last two terms of Eq. 2, leads to the blue asymmetry for the bands. Here, \( \beta_r \) may be neglected, since \( \beta_r < D_r \ll \alpha_r \).

The radiative flux \( S \) for a rotational line of the fundamental series \((r + 1 \rightarrow r)\) Stokes Raman-scattered Q-branch is given by (9, 10)

\[
S(r, J) \propto \frac{(J + 1)}{Q_m} \exp \left(-\frac{2\epsilon}{kT}G(r, J)\right) \tag{3}
\]

where \( k \) is Boltzmann's constant and \( \omega_r \) is the wave number of the Raman fundamental line (11):

\[
\omega_r = \nu_o - \Delta \nu(r + 1, r + 1 - \nu)
\]

for which \( \omega_r \) is the wave number of the incoming (laser) radiation. Here, the depolarized contribution has been neglected, and the factors associated with the cross section which are not explicitly written out are denoted by \( c_r \).

The rotational (12) and vibrational partition functions \( Q_m \) and \( Q_v \) are, respectively,

\[
Q_m \sim kT/2\hbar^2B
\]

\[
Q_v \sim [1 - \exp (-\hbar c_r/kT)]
\]

and the factor \( \eta \) accounts for the effect of nuclear spin \( J \). For \( N_2 \) \((f = 13)\), the parity of the rotational levels is such that the symmetric levels correspond to even values of \( J \), for which \( \eta = 1 \), whereas the antisymmetric levels correspond to odd values of \( J \), for which \( \eta = \frac{1}{2} \). For \( O_2 \) \((f = 0)\), the symmetric levels correspond to odd values of \( J \), for which \( \eta = 1 \), whereas the antisymmetric levels correspond to even values of \( J \), for which \( \eta = 0 \) (that is, the lines corresponding to even values of \( J \) are missing).

It is evident from Eq. 3 that the shape of each particular band (that is, a given \( \nu \) of the fundamental series) will be dependent upon the rotational temperature, and that a proper fit to an experimental profile can then serve to determine this temperature. All of the bands of the fundamental series will have somewhat similar shapes. Here, for the purposes of illustration, we consider the ground-state band. The shape of this band (that is, the \( S \) versus \( \nu \) profile) may be calculated from Eq. 3 which, for a fixed temperature, becomes

\[
S(J) \propto (2J + 1) \exp (-2\nu_o/\hbar c_r/kT)
\]

with

\[
\omega_r = \nu_o - 2\omega_r + \omega_r(3r^2 + 6r + 13/4) - \alpha_JU + 1 - \beta_r(I + 1)^4 + \ldots
\]

where only those terms of quantitative significance which contribute to the relative band shape have been retained. The partition functions provide only a
temperature-dependent scale factor for Eq. 3, and so are not of concern for profile fitting.

The experiments reported here corresponded with reasonable certainty to equilibrium populations for the vibrational and rotational energy levels. However, for situations in which equilibrium is not expected, the temperature factors appearing in the exponents of Eq. 3 can be denoted as values of $T_{\nu\mu}$ or $T_{\nu\mu\tau}$ associated with particular energy levels, and the vibrational and rotational excitation ten tests corresponding to these degrees of freedom can therefore be determined. In general, the relative peak value or integrated intensity of each successively indicates the vibrational temperature, whereas the shape (that is, blue asymmetry) of each band determines the rotational temperature. Thus, if nonequilibrium is suspected, separate fits to the shape of each band should be made. In this fashion, different vibrational and rotational excitation temperatures can be associated with each internal mode. This method should complement the well-studied OH emission and absorption techniques for the measurement of excitation temperatures, which have been applied to flames with success (13); conversely, this method might serve to determine anharmonic terms for species that have not yet been well studied (14).

For the case where equilibrium exists, relative values of $S(\nu, J)$ can be calculated as a function of wavelength over the entire spectral extent of the scattered bands for various temperatures and the results fitted to experimental curves. This has been done (15) for $\text{N}_2$ and $\text{O}_2$ in Figs. 3 and 4, with the result that the $\text{N}_2$ data closely fit 1600 K and the $\text{O}_2$ data roughly fit 1700 K. These values are reasonable for the flames used. We believe that these results demonstrate the utility of this Raman scattering method for the determination of these temperatures, as well as for temperatures in a variety of other experimental and practical areas.

For $\text{H}_2\text{O}$, the analytical results are considerably more complicated since the calculations involve asymmetric top energy levels (16). However, if we consider only the purely vibrational contributions to the energy levels for an anharmonic non-linear triatomic molecule (17), we can investigate a qualitative fashion the lowest possible upper-state bands, where we use the notation $(\nu_1, \nu_2, \nu_3)$ to denote the vibrational quantum numbers for the three fundamental vibrational modes. If band corresponding to the transition $(1,1,0)-(0,1,0)$ is the most likely to be observed, since it arises from the population of the lowest excited vibrational level ($\nu_1 = 1.0, 0.0$ ev above the ground state). The separation $\Delta \nu$ between the upper-state band and the ground-state band for no rotation is $-\Delta \nu_0$, where $\Delta \nu_0$ is the coefficient of the $(\nu_1 + 15) (\nu_2 + 15) (\nu_3 + 15)$ term in the energy level expression. For $\text{H}_2\text{O}, \Delta \nu_0 = -20.0 \, \text{cm}^{-1}$ and $\Delta \nu$ corresponds to a blue shift of 7.05 Å for incident 4880 Å radiation. This shift closely coincides with the position of feature (b) in Fig. 2A (since $\nu_0$ is located slightly to the right of the peak of the Raman scattering curve in Fig. 2B). Thus, we have evidence of an appreciable population of the $\text{H}_2\text{O}$ $v_3 = 1$ level for the flame studied. More importantly, this result demonstrates the potential ability of Raman scattering measurements for polyatomic molecules.

In this report we have concentrated on temperature measurements. However, there is also substantial interest in the use of Raman scattering as a constituency probe in flames and other systems. One important point concerning such measurements is illustrated by the foregoing results. For systems wherein significant vibrational and rotational excitation occurs, temperature-dependent calculations, such as the ones we have discussed, are necessary (in addition to the basic cross section) in order to relate the scattering intensity over any specified bandwidth to the concentration of a particular constituent. Otherwise, significant errors in concentration analyses may be made, particularly in view of the fact that the total Q-branch scattering becomes $v_3$ in the upper-state band scattering.

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References and Notes

1. In other literature on Raman scattering and as defined work these bands are often called hot bands, in reference to their appearance under thermally excited conditions. However, this phrase can be misleading, since upper state bands can appear at low temperature for species with low-lying vibrational energy levels. For example, Hollow et al. (7) have shown the importance of upper-state bands in $\nu_3$ at room temperature. We have adopted the phrase "vibrational band" from R. M. Gorby [Atmospheric Radiation, vol. 1, Tho- rni, edited by R. J. H. Grogan (Plenum Press, London, 1978) p. 21]. One further point of possible confusion lies in the commonly used term "vibrational band" for the ground-state fundamental band. This is misleading, since the band is not necessarily narrow Q-branches observed at room temperature, and so is not used here.


5. See, for example, W. E. Knab, in Sixth Symposium (International) on Combustion, Cleveland, Ohio, 1959, p. 655.


7. The essential results apply for the case of a schematic molecular band (16), with experimental results. Calculations for polyatomic molecules are necessarily more complicated.

8. G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, Princeton, N.J., ed. 2, 1950), chap. 3. The spectroscopic constants for $\text{N}_2$ and $\text{O}_2$ were taken from table 39.


11. In this development, the usual number $n_0$ is a function of both $J$ and $N$, and $J = 1$ and $N = 0$ is the wave number is not simply the reciprocal of $a_0$, but is defined in the wave number corresponding to $J = 0$ for the ground-state vibrational band.

12. The rotational partition function given here is evaluated for a 2-3 state of 3-homogeneous species in the ground state for both $\text{N}_2$ and $\text{O}_2$. It includes the effect of nuclear spin.$^{(a)}$


15. Calculated results for the bands in Figs. 3 and 4 were obtained from the convolution of $S(\nu, J)$ values from Eq. 3 with the experimentally determined molecular density function, which indicates the relative response of the monochromator to the wave number of which it is set at. These calculations were carried out through use of a computer. The function was found to be fitted by an expression of the form $e^{-\Delta E/\kappa}$, where $\Delta E$ is the energy difference between the upper and lower state, and $\kappa$ is the width of the band.

16. This work was supported in part by the National Science Foundation under Grant No. 77-71.


19. In this work, for example, the $J$ values used, 3 and 4, were obtained from the convolution of $S(\nu, J)$ values from Eq. 3 with the experimentally determined molecular density function, which indicates the relative response of the monochromator to the wave number of which it is set at. These calculations were carried out through use of a computer. The function was found to be fitted by an expression of the form $e^{-\Delta E/\kappa}$, where $\Delta E$ is the energy difference between the upper and lower state, and $\kappa$ is the width of the band.
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