

Raman Scattering from Water Vapor in Flames

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Theme

WE report an experimental investigation of the vibrational Raman scattering signature for water vapor, a technologically important species in combustion, with emphasis on the broad spectra obtained from flames at about 1500 K. These data are contrasted to the relatively narrower spectra for other simple molecules, such as nitrogen, and for water vapor at lower temperatures. The implications of these broad spectra upon temperature and density measurements are discussed.

Contents

Vibrational Raman scattering (VRS) measurement techniques are potentially of significant use in probing advanced combustion systems, which often present a hostile environment for physical probes (see, for example, Ref. 1). Here, we present experimental results for the water vapor VRS signature under flame conditions.

Raman scattering density measurements are based upon the scattered intensity from the molecule under consideration, while the corresponding temperature measurements are based upon the sensitivity of the scattering profiles to temperature. The basic method for VRS temperature diagnostics involves either performing a fit of an experimental contour to a theoretical temperature-sensitive profile, or taking the ratio of experimental data in selected temperature-sensitive regions of the spectrum. Of particular interest here are temperature-measurement methods based upon utilizing various portions of the vibrational Stokes Q -branch fundamental band series contour; these have been used for flame measurements, most prominently on N_2 , by a number of workers (see, for example, Ref. 2).

Temperature measurements utilizing vibrational Stokes band peak intensity ratios or curve fitting are applicable to many molecules other than nitrogen, with the only requirement being that the vibrational scattering profile must be either predictable analytically or correlated with detailed experimental results as a function of temperature. For example, Leonard,³ Nelson et al.,⁴ and Lapp et al.⁵ have measured CO_2 temperatures; Setchell⁶ has obtained measures of CO as well as N_2 temperature; Lapp et al.⁷ have measured O_2 temperatures; and Setchell⁶ and Lapp² have determined values of temperature from H_2 .

Temperature measurements utilizing water vapor are considerably more complicated than for nitrogen, since theoretical calculation of the vibrational scattering contour for this asymmetric top molecule is more difficult than for simpler molecules of higher symmetry. A program under way with Gaufres and co-workers (Montpellier, France) to understand better the Raman band profiles of water vapor has yielded detailed results with good agreement between experiment and theory over the low-temperature range of 150 to

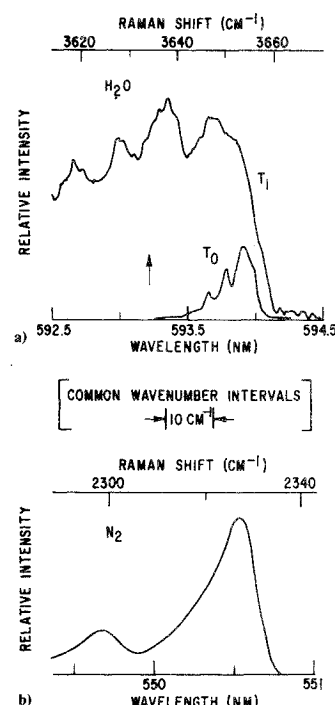
350°C.⁸ Recently, agreement has also been demonstrated with the experimental flame data shown here⁹; further details of this calculation will appear elsewhere. Additionally, low-resolution VRS water-vapor data obtained by Miller et al.¹⁰ were shown to be in reasonable accord with theoretical estimates at flame temperatures.

The experimental Raman band contour flame data shown in Fig. 1a were obtained through use of 1.05 W of 488-nm radiation from an argon ion laser. The scattered light was analyzed by a Spex Model 1400-II, $\frac{3}{4}$ m, scanning double monochromator using 1200 ℓ/mm Bausch and Lomb gratings blazed at 500 nm. The radiation was detected by an RCA Model C31000E photomultiplier cooled to -50°C , with subsequent photon-counting electronics and data-logging techniques.

A hydrogen-oxygen flame close to stoichiometric was used for this study. The flame was produced horizontally on a 2.5-cm diam. water-cooled porous plug burner which was burning into another water-cooled porous plug 2.0-cm distant.² The equivalence ratio (i.e., the fuel-to-oxidizer ratio divided by this ratio at stoichiometric) was 1.07, and the total flow rate was 73.4 cm^3/sec . Some entrainment of air into the flame was possible, and this permitted a temperature measurement from the nitrogen Stokes vibrational Raman profile. The Raman data (from band peak ratios) gave 1527 K, with a somewhat lower value for a least-square curve fit. For purposes of comparison, we also show water vapor data taken at room temperature in Fig. 1a.¹¹

That the water vapor vibrational band at the flame temperatures studied is extremely broad can be seen in Fig. 1a. Additional data indicate that the entire contour is about twice as broad as the major part shown in Fig. 1a, and that this tail

Fig. 1 a) Curve T_1 : Experimentally observed Stokes vibrational Raman spectrum of water vapor (ν_1 -band contour) from hydrogen-oxygen flame at roughly 1500 K, for a 488-nm laser source and triangular monochromator spectral slit function with 0.162 nm ($\sim 4.6 \text{ cm}^{-1}$) FWHM. Vertical arrow corresponds to spectral vicinity in which first upper state vibrational band is expected. **Curve T_0 :** Same band contour for water vapor in test cell at 24°C , using triangular slit function with 1.8 cm^{-1} FWHM.¹¹ Note that the relative intensity scales for curves T_1 and T_0 are unrelated. **b) Calculated Stokes vibrational Q -branch contour for nitrogen at 1500 K** for triangular monochromator slit function with 0.163 nm ($\sim 5.4 \text{ cm}^{-1}$) FWHM.² The Raman profiles shown in parts a and b are plotted for common wavenumber intervals.



Received Nov. 21, 1974; presented as Paper 74-1143 at AIAA/SAE 10th Propulsion Conference, San Diego, Calif., Oct. 21-23, 1974; synoptic received Feb. 14, 1977; revision received Aug. 17, 1977. Full paper available from AIAA Library, 750 Third Avenue, New York, N.Y. 10017. Price: Microfiche, \$2.00; hard copy, \$5.00. Order must be accompanied by remittance.

Index categories: Experimental Methods of Diagnostics; Sensor Systems; Combustion and Combustor Designs.

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falls off in intensity as a roughly linear extrapolation. We note particularly that the water vapor band is significantly wider under flame conditions than at room temperature, by a factor of about 6, and is also significantly broader than a nitrogen contour at approximately the same temperature (see Fig. 1b).

This strong temperature dependence of vibrational Raman scattering is not only of significance for temperature measurements, but also has a profound influence on density measurements. First, density measurements from Raman scattering signatures are based upon the fact that the total scattered intensity is linearly proportional to the species density. The proportionality factor for vibrational Raman scattering is effectively independent of temperature for temperatures below which appreciable vibrational excitation is found. At higher temperatures (e.g., in flames) this factor develops a temperature dependence that must be measured or calculated in order to obtain accurate density data.[†]

Second, the utilization of any monochromator or filter bandpass which is fixed in spectral extent implies that the observed Raman signal will correspond to varying fractions of the total water vapor band intensity if measurements are made at various temperatures, unless the bandpass is initially set to include the total band at the highest temperature to be encountered. These fractions will depend (as a function of temperature) upon both the spectral bandpasses and the positions of the bandpass centers.

The two effects described can be of opposite sense; i.e., the total scattering in a vibrational band increases with temperature, but the fraction of this scattering that gets through a restricted bandpass can decrease because the band spreads with increasing temperature. Over some temperature ranges it can be possible to choose a bandpass such that these effects nearly cancel, producing a density measurement nearly independent of temperature,^{8,12} a desirable result for the design of efficient measurement techniques.

Another major implication of the spectral extent of the water vapor signature is the possibility of the contour masking the Q-branch of another species which may be present in amounts small compared to the water vapor concentration. An example of such a species is the radical OH, whose ground-state band is located at 591 nm (for 488-nm irradiation). This wavelength is located in the tail of the water band, and this tail will presumably grow in intensity as the

temperature is increased (i.e., as conditions become more favorable for the formation and observation of OH).

Acknowledgment

The author is grateful to C.M. Penney for his valuable collaboration, and to F.F. Haller for his help with the computer data logging system. This work was supported in part by Project SQUID, Office of Naval Research.

References

- ¹Lapp, M. and Penney, C.M., "Raman Measurements on Flames," *Advances in Infrared and Raman Spectroscopy*, Vol. 3, edited by R.J.H. Clark and R.E. Hester, Heyden and Son Ltd., London, 1977, pp. 204-261.
- ²Lapp, M., "Flame Temperatures From Vibrational Raman Scattering," *Laser Raman Gas Diagnostics*, edited by M. Lapp and C.M. Penney, Plenum Press, New York, 1974, pp. 107-145.
- ³Leonard, D.A., "Development of a Laser Raman Aircraft Turbine Engine Exhaust Emissions Measurement System," AVCO Everett Research Laboratory, Research Note 914, 1972.
- ⁴Nelson, L.Y., Saunders, A.W., Harvey, A.B., and Neely, G.O., "Detection of Vibrationally Excited Homonuclear Diatomic Molecules by Raman Spectroscopy," *Journal of Chemical Physics*, Vol. 55, Nov. 1971, pp. 5127-5128.
- ⁵Lapp, M., Penney, C.M., and Goldman, L.M., "Vibrational Raman Scattering Temperature Measurements," *Optics Communications*, Vol. 9, Oct. 1973, pp. 195-200.
- ⁶Setchell, R.E., "Time-Averaged Measurements in Turbulent Flames using Raman Spectroscopy," AIAA Paper 76-28, 1976; also, "Analysis of Flame Emissions by Laser Raman Spectroscopy," Sandia Laboratories, Energy Report No. SLL74-5244, 1974.
- ⁷Lapp, M., Goldman, L.M., and Penney, C.M., "Raman Scattering from Flames," *Science*, Vol. 175, March 1972, pp. 1112-1115.
- ⁸Bribes, J.L., Gaufres, R., Monan, M., Lapp, M., and Penney, C.M., "Raman Band Contours for Water Vapor as a Function of Temperature," *Applied Physics Letters*, Vol. 28, March 1976, pp. 336-337.
- ⁹Bribes, J.L., Gaufres, R., Monan, M., Lapp, M., and Penney, C.M., "Detailed Study of the Q-Branch Profile of the ν_1 of Water Molecule from 293°K to 1500°K," *Proceedings of the Fifth International Conference on Raman Spectroscopy*, edited by E.D. Schmid et al., Universität Freiburg, Sept. 2-8, 1976, Hans Ferdinand Schulz Verlag, Freiburg im Breisgau, 1976.
- ¹⁰Miller, P.J., Modestino, A.J., and Klainer, S.M., "Laser Raman Study of Water Vapor," Arnold Engineering Development Center, AEDC-TR-75-150, 1975 (available from Defense Documentation Center).
- ¹¹Penney, C.M. and Lapp, M., "Raman-Scattering Cross Sections for Water Vapor," *Journal of the Optical Society of America*, Vol. 66, May 1976, pp. 422-425.
- ¹²Leonard, D.A., "Point Measurement of Density by Laser Raman Scattering," Project SQUID (Office of Naval Research) TR AVCO-1-PU, 1972.

[†]This temperature-dependent factor for the integrated vibrational Q-branch intensity of a diatomic molecule is approximately given by the vibrational partition function for thermal equilibrium conditions.⁵

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