

Rotational Temperature Measurement in High-Temperature Air using KrF Laser-Induced O₂ Fluorescence

J. H. Grinstead, G. Laufer, J. C. McDaniel, Jr.

Aerospace Research Laboratory, University of Virginia, 570 Edgemont Road, Charlottesville, VA 22903, USA
(Fax: +1-804/982-5357, e-mail: jhg4b@virginia.edu)

Received 13 May 1993/Accepted 18 August 1993

Abstract. Rotational temperature of O₂ has been measured in an atmospheric-air furnace using KrF laser-induced fluorescence. Average measurement errors of 10.7% and 5.1% over a temperature range of 1325–1725 K were observed using two- and four-line excitation techniques, respectively. Ground-state depletion was observed for a spectral laser irradiance greater than approximately $7.5 \times 10^6 \text{ W/cm}^2 \text{ cm}^{-1}$. This technique is suitable for temperature measurements when the O₂ vibrational population is not in thermal equilibrium.

PACS: 07.60, 33.50

Laser-induced O₂ fluorescence is a particularly attractive technique for spatially resolved measurements of temperature in high-speed reacting and nonreacting air flows. Since O₂ is naturally present in air, no seed species is necessary. Narrowband ArF- and KrF-excimer lasers and dye-laser systems can be used for the selective excitation of ro-vibronic transitions in the $B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann-Runge system of O₂ [1–3]. The resulting fluorescence signal is proportional to the population density of the absorbing state which, in turn, depends on the gas temperature and density.

An O₂ LIF technique which is useful when conditions of vibrational nonequilibrium at high temperature are present was identified [4]. With this technique a tunable KrF laser is used for O₂ rotational temperature measurement. The measurement of temperature using laser-induced O₂ fluorescence requires that the sample volume be in thermal equilibrium. Unfortunately, homonuclear molecules such as O₂ do not have permanent dipole moments in the ground electronic state. Therefore, relaxation of vibrational nonequilibrium occurs primarily by collisions. In high-speed flows where large gradients may induce local nonequilibrium conditions, vibrational relaxation may occur over distances comparable to the characteristic length scale of the flowfield. Since the collisional relaxation time for the rotational energy levels is much shorter than the relaxation time for the vibrational levels, it is expected that the rotational energy distribution will reach

equilibrium long before the vibrational distribution. As a result, the rotational temperature – the temperature defined by the population distribution among rotational levels within a single vibrational level – will be well-defined even in the absence of vibrational equilibrium and may be considered to be a reasonable approximation of the true equilibrium temperature.

Measurement of rotational temperature requires that the relative population densities of two or more rotational states within the same vibrational level be determined; therefore, the transitions excited must originate from the same vibrational level. If the excitation of each of these transitions is free from inadvertent excitation of an adjacent vibrational level, the relative fluorescence signals will be independent of the vibrational population distribution and, assuming a Boltzmann distribution among the rotational levels, will depend only upon the rotational temperature. Otherwise, if two or more vibrational levels are involved in the excitation, effects of vibrational nonequilibrium may introduce a systematic error of unknown magnitude.

Pure O₂ rotational temperature measurements were previously demonstrated using a narrowband ArF laser [5, 6]. However, at temperatures exceeding 800 K coincident excitation of more than one ground vibrational level cannot be avoided using an ArF laser [4]. Therefore, measurements with an ArF laser under conditions of vibrational nonequilibrium may be subject to systematic errors. By contrast, excitation of ro-vibronic transitions in the 0–6 band using a tunable KrF can be isolated from excitations of other vibrational levels. Because of a favorable fluorescence yield [7–9], the fluorescence induced by the excitation of $v''(6)$ was found to be sufficient for point measurements in atmospheric pressure air at vibrational temperatures exceeding 1250 K. Furthermore, in reacting flows where the temperature is normally higher than 1250 K, LIF measurements may be feasible even as the oxygen is being consumed by the reactions. Oxygen LIF using a KrF laser has been demonstrated experimentally in combusting environments [2, 10, 11]. The conditions for obtaining quantitative measurements of KrF laser-induced O₂ fluorescence have been determined theoretically and experimentally [12]. Spectroscopic mea-

measurements have also demonstrated that the $v''(6)$ state can be excited without inadvertent excitation of adjacent vibrational states. Here we demonstrate experimentally the use of a tunable KrF laser for O_2 LIF rotational temperature measurements in high-temperature atmospheric air. Although in these experiments the air was at thermal equilibrium, we have demonstrated before [12] that rotational temperature measurements using selected transitions in the 0–6 band are independent of the vibrational temperature; i.e. that rotational temperature measurement is possible in the presence or absence of vibrational equilibrium. On the other hand, equilibrium is required if comparison with standard temperature measurement techniques is desired.

An atmospheric air furnace maintained at steady and uniform temperatures up to 1850 K was used as the source of high-temperature O_2 . Independent temperature measurements were obtained by a 0.1 mm Pt+30% Rh/Pt+6% Rh monitoring thermocouple. The furnace was modified for optical access with insulated tubular 12 mm openings ($l/d = 11$) through two opposite walls and an insulated conical observation opening through a third wall. The monitoring thermocouple was placed 3 mm off axis from the laser beam and along the collection axis. The radiative view factor from the thermocouple to the external atmosphere through the optical access ports was less than 10^{-3} . From this, the systematic temperature measurement error due to radiative heat losses through the optical access ports was estimated to be less than 1°C at the maximum temperature studied (1800 K). Random fluctuations in the temperature measurement were less than 5°C . No corrections were made for the minor radiative losses and fluctuations.

The laser used was an injection-locked, narrowband tunable KrF laser radiating nominally at 248 nm with a pulse energy of approximately 175 mJ. A motor-driven micrometer equipped with a piezo-electric transducer tip was mounted to the oscillator diffraction grating. This permitted continuous wavelength selection over the tuning range of the laser. The linewidth of the laser was approximately 0.5 cm^{-1} . The laser was focused into the furnace by a spherical 750 mm focal-length lens. The cross-section of the beam at the point of fluorescence measurement was measured to be $2.5\text{ mm} \times 5\text{ mm}$. Except when depletion of the ground state was studied, the pulse energy was kept below 15 mJ at the point of fluorescence measurement. The fluorescence was imaged with $f/8$ optics onto a photomultiplier tube fitted with a BG 37 glass filter and a 10 nm bandpass filter centered at 351 nm. A gated boxcar integrator and a computer were used for data acquisition.

Excitation spectra of the 0–6 band of O_2 in atmospheric air excited by a KrF laser were obtained at various furnace temperatures between 1325 K and 1725 K. The bandpass filter transmits fluorescence primarily of the 0–15 band. Dispersion spectra obtained following the excitation of rotational lines in the 0–6 band showed well-resolved emission lines from the laser-excited rotational state, thereby confirming that collisional redistribution of the excited rotational state is negligible.

Rotational temperature measurements in the furnace were obtained using two- and four-line excitation approaches. The peak fluorescence values of the 0–6 $P(7)$, $P(9)$, $P(15)$, and $R(17)$ lines were measured from the excitation spectra.

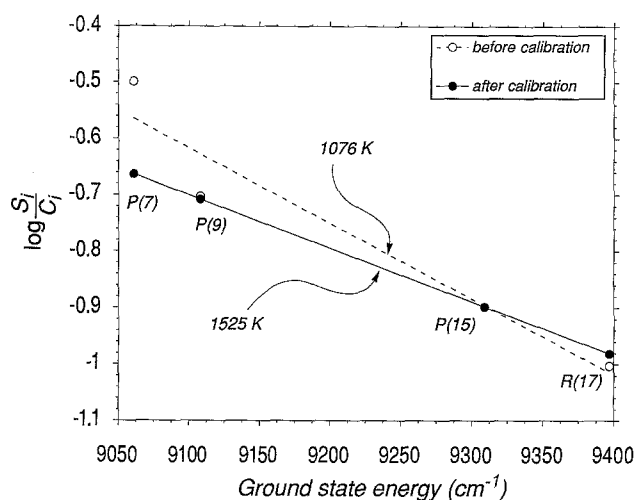


Fig. 1. Boltzmann plot for four O_2 0–6 transitions at a thermocouple temperature of 1525 K. The open circles correspond to the fluorescence measurements S_i and normalization constants C_i determined by available spectroscopic data. The filled circles correspond to normalization by experimentally-determined normalization constants at this temperature

Of these four, only the $P(7)$ and $R(17)$ transitions are spectrally isolated from transitions from $v''(7)$ [12]. The $P(9)$ and $P(15)$ lines slightly overlap transitions from $v''(7)$. However, calculations show that for thermal equilibrium at 1800 K the fluorescence resulting from excitation of $v''(7)$ accounts for less than 1% of the fluorescence detected by our system when the laser is tuned to either the $P(9)$ or $P(15)$ transitions. This observation indicates that spurious excitation of $v''(7)$ will have negligible influence on the $v''(6)$ rotational temperature measurement when the $P(9)$ and $P(15)$ lines are excited and no influence when the $P(7)$ and $R(17)$ lines are excited, even in a vibrationally unrelaxed system. For comparison, rotational temperatures were determined both from a Boltzmann plot for the peak fluorescence values of the four lines and from the ratio of the peak fluorescence values of the $P(7)$ and $R(17)$ lines.

Figure 1 presents a Boltzmann plot of the four 0–6 absorption lines at a thermocouple temperature of 1525 K. The peak fluorescence values S_i were measured from an excitation spectrum obtained at that temperature and represent 5-pulse averages. For a Boltzmann plot, the fluorescence signal is divided by a normalization constant C_i . This constant is the product of the appropriate Hönl-London factor (rotational line strength) and the radiative decay rate divided by the predissociation rate of the laser-excited state. On a semi-log plot, the slope of a straight line passed through these points represents the inverse temperature dependence of the exponential factors in the Boltzmann population fractions for the initial states. The open circles of Fig. 1 were obtained by dividing the measured fluorescence values by a normalization constant calculated using available data [7, 9, 13]. A linear fit to these points results in a temperature of 1076 K – approximately 29% lower than the measured thermocouple temperature. Using the ratio of the $P(7)$ and $R(17)$ lines, a temperature of 970 K was obtained. This discrepancy was attributed to uncertainties in the reported spectroscopic constants for $v''(0)$ and in some of the experimental param-

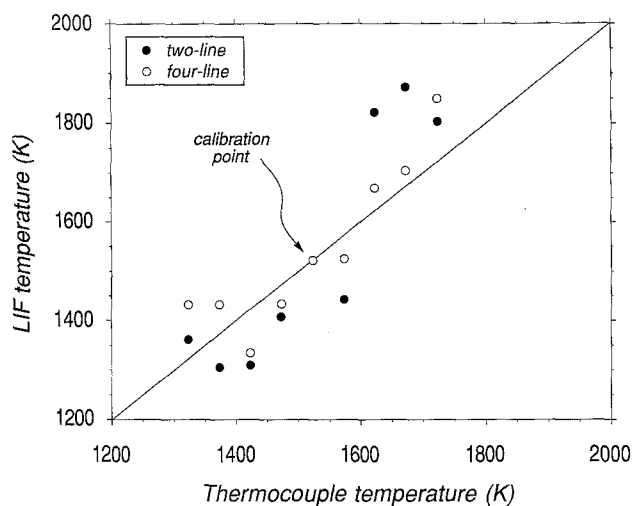


Fig. 2. Comparison of thermocouple and LIF temperature measurements in atmospheric air. For the four-line measurements, the 0–6 $P(7)$, $P(9)$, $P(15)$, and $R(17)$ lines were used. For the two-line measurements, the $P(7)$ and $R(17)$ lines were used

eters; e.g., spectral transmission of the bandpass filter and variations of laser locking efficiency with wavelength (particularly in the case of the $P(7)$ line, which lies near the end of the tuning range). Because of these uncertainties, the constants C_i required for the normalization of the peak fluorescence intensity of each excitation line were determined experimentally at this thermocouple temperature; the filled circles of Fig. 1 show the Boltzmann plot obtained by dividing S_i by the experimentally-determined correction factor. For the $P(15)$ line, this factor was arbitrarily selected to be unity. The magnitude of the correction factor for each of the remaining lines is represented by the vertical separation between the filled and open circles in Fig. 1. The $P(7)$ – $R(17)$ two-line temperature measurement technique was calibrated in an analogous manner at this same temperature. Subsequent temperature measurements were obtained using the measured fluorescence values and the constants obtained from this calibration. Figure 2 presents a comparison between the O_2 LIF and thermocouple temperature measurements obtained at various furnace temperatures for the two- and four-line techniques. Excluding the calibration point at 1525 K, the r.m.s. errors of the LIF measurements were 10.7% and 5.1% for the two- and four-line techniques, respectively.

The uncertainty in the measurements may be projected from the measured Signal-to-Noise Ratios (SNR) of the fluorescence values. For the two-line technique, the fractional uncertainty in the temperature measurement $\Delta T/T$ can be written as [12]:

$$\frac{\Delta T}{T} = \frac{\Delta R}{R} \frac{kT}{\Delta E}, \quad (1)$$

where $\Delta R/R$ is the fractional uncertainty in the ratio of the two fluorescence values, k is Boltzmann's constant, and ΔE is the energy separation of the ground states of the two transitions. The variation of the temperature measurement uncertainty was calculated analytically for two hypothetical

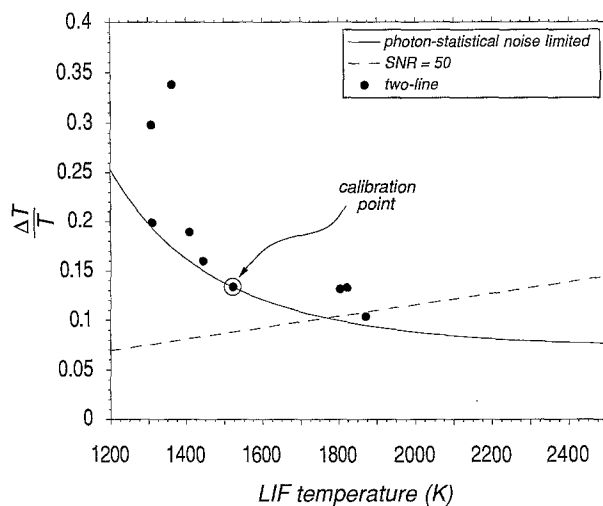


Fig. 3. Predicted temperature measurement uncertainties for two-line excitation. The solid line represents a measurement uncertainty for fluorescence measurements that are limited by photon-statistical noise. The dashed line corresponds to a constant fluorescence measurement signal-to-noise ratio of 50. The filled circles are the predicted uncertainties of the two-line measurements in Fig. 2 based on measured signal-to-noise ratios

cases. In the first case, represented in Fig. 3 by the solid line, the fluorescence measurement uncertainty was assumed to be limited by photon-statistical noise. In the second case (dashed line), the SNR was maintained at 50 throughout the temperature range. When limited by photon-statistical noise, the SNR is equal to $\sqrt{S_i}$. For this case, the measurement uncertainty decreases with increasing temperature and is seen to approach a value of approximately 7% at 2500 K. The measurement uncertainty using the four-line technique is expected to be smaller than the two-line technique for all temperatures. For comparison, the measurement uncertainty of the two-line technique was evaluated using (1) and the measured fluorescence signal-to-noise ratios and is shown by the points in Fig. 3. The measured uncertainty is seen to follow the solid line, thereby suggesting that our experiments were limited by photon-statistical noise. We also observe that the measured error in Fig. 2 is well within the measurement uncertainty projected in Fig. 3.

Although the measurement accuracy of the technique is limited by the photon-statistical noise, the temperature measurement sensitivity is determined by the energy separation of 336 cm^{-1} between the ground states of the 0–6 $P(7)$ and $R(17)$ transitions. This separation corresponds to a rotational temperature of 484 K, which is small relative to the measured temperatures. Therefore, the temperature sensitivity of the fluorescence signal ratio of these lines is low. As seen in (1), a smaller energy separation results in a higher measurement uncertainty. However, no other sufficiently isolated rotational transitions in the 0–6 band with larger ground state energy separations were accessible within the tuning range of the laser.

The measurement accuracy may be improved by reducing the photon-statistical noise. This, in turn, could be achieved by increasing the incident laser irradiance. However, due to the large absorption cross-sections for these transitions and the high predissociation rate of the excited states, ground state depletion is possible even for moderate laser irradi-

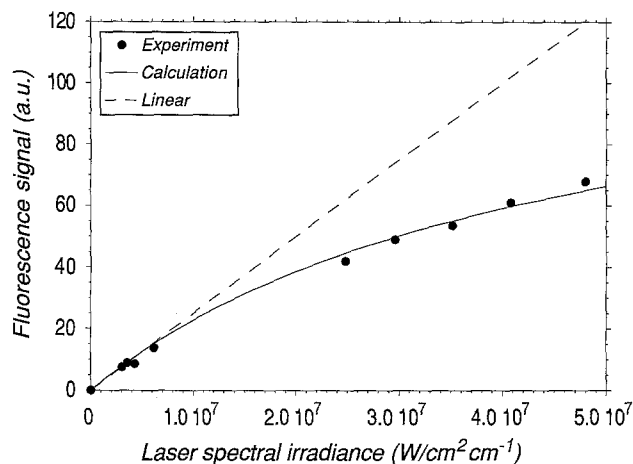


Fig. 4. Experimental and calculated variation with incident laser intensity of the fluorescence signal resulting from excitation of the 0–6 $R(17)$ transition of O_2 in atmospheric air at 1475 K

ances. The effect of the incident laser irradiance on the population of the probed state was determined experimentally and theoretically. The variation with laser irradiance of the fluorescence signal resulting from the excitation of the 0–6 $R(17)$ line at an air temperature of 1425 K was measured, and the results are shown by the points in Fig. 4. The fluorescence signal was found to increase linearly with laser spectral irradiance when the spectral irradiance was below approximately $7.5 \times 10^6 W/cm^2 cm^{-1}$, which corresponds to a fluence of $150 mJ/cm^2$ for an absorption linewidth of $0.4 cm^{-1}$. However, at larger spectral laser irradiances the fluorescence signal exhibited nonlinear behavior. For comparison the variation of the fluorescence signal with laser intensity was calculated using a time-dependent model of the LIF process, and the results are shown by the solid line in Fig. 4. The model includes the initial and excited ro-vibrational states coupled by the laser and a bath level of rotational states within the initial vibrational level, $v''(6)$. Because of the long lifetime of the thermally-excited vibrational states in comparison with the pulse duration of the laser, vibrational energy transfer between $v''(6)$ and adjacent vibrational levels could be neglected. The good agreement between the calculated and measured variation of fluorescence intensities suggests that the nonlinear variation of the fluorescence signal can be attributed primarily to depletion of the population in $v''(6)$, which, as assumed in the calculation, cannot be replenished within the pulse duration by population transfer from adjacent vibrational levels.

Rotational temperature measurement using KrF laser-induced O_2 fluorescence has been demonstrated in a high-temperature atmospheric air furnace. Transitions in the 0–6 band were excited, and the rotational temperature was determined from Boltzmann plots and an independent calibration at 1525 K. Based upon 5-pulse averaging, an r.m.s. measurement error of 5.1% using four-line excitation was shown for the temperature range of 1325–1725 K. An r.m.s. error of 10.7% was observed with two-line excitation. When the measurement is limited by photon-statistical noise, the temperature measurement uncertainty for the two-line excitation technique approaches 7% at high temperatures. Since the rotational lines from $v''(6)$ excited for these measurements were isolated from lines from adjacent vibrational states, this LIF technique is useful also when the vibrational population distribution departs from equilibrium. Depletion of the ground state by the incident laser beam was determined experimentally and theoretically to be negligible for laser spectral irradiances below approximately $7.5 \times 10^6 W/cm^2 cm^{-1}$.

Acknowledgements. This work was supported by NASA grant NAG-1-795 from the Langley Research Center, USA. The continued interest and support of Dr. G. Burton Northam, the technical monitor at Langley, are greatly appreciated.

References

1. K. Shibuya, F. Stuhl: *J. Chem. Phys.* **76**, 1184 (1982)
2. P. Andresen, A. Bath, W. Gröger, H.W. Lülf, G. Meijer, J.J. ter Meulen: *Appl. Opt.* **27**, 365 (1988)
3. J.E.M. Goldsmith, R.J.M. Anderson: *Opt. Lett.* **11**, 67 (1986)
4. J.H. Grinstead, G. Laufer: ICIASF '91 Record, Int'l Conf. on Instrumentation for Aerospace Simulation Facilities (IEEE, New York 1991) p. 262
5. G. Laufer, R.L. McKenzie, D.G. Fletcher: *Appl. Opt.* **27**, 4873 (1990)
6. D.G. Fletcher, R.L. McKenzie: *Opt. Lett.* **17**, 1614 (1992)
7. P.H. Krupenie: *J. Phys. Chem. Ref. Data* **1**, 423 (1972)
8. A.S.-C. Cheung, K. Yoshino, J.R. Esmond, S.S.-L. Chiu, D.E. Freeman, W.H. Parkinson: *J. Chem. Phys.* **92**, 842 (1990)
9. P.C. Cosby, H. Park, R.A. Copeland, T.G. Slanger: *J. Chem. Phys.* **98**, 5117 (1993)
10. A. Arnold, W. Ketterle, H. Becker, J. Wolfrum: *Appl. Phys. B* **51**, 99 (1990)
11. P. Andresen, H. Schlüter, D. Wolff, H. Voges, A. Koch, W. Hentschel, W. Opperman, E. Rothe: *Appl. Opt.* **31**, 7684 (1992)
12. J.H. Grinstead, G. Laufer, J.C. McDaniel, Jr.: AIAA 93-0045, AIAA 31st Aerospace Sciences Meeting, Reno, NV (1993)
13. G. Herzberg: *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (Van Nostrand, New York 1950) p. 208