NRC Publications Archive Archives des publications du CNRC

Precision of multiplex CARS temperatures using both single-mode and multimode pump lasers

Snelling, D. R.; Smallwood, G. J.; Sawchuk, R. A.; Parameswaran, T.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Applied Optics, 26, 1, pp. 99-110, 1987

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=1304bff5-a0d1-4bab-bfdb-1c3a97a24955>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=1304bff5-a0d1-4bab-bfdb-1c3a97a24955>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Precision of multiplex CARS temperatures using both single-mode and multimode pump lasers

D. R. Snelling, G. J. Smallwood, R. A. Sawchuk, and T. Parameswaran

The noise level in single-pulse resonant nitrogen CARS spectra is shown to decrease with increasing pump laser bandwidth. This is the reverse of the trend observed for nonresonant CARS spectra. The precision of single-pulse CARS temperature measurements is shown to be dramatically increased by performing a weighted fit of theoretical and experimental CARS spectra using the measured detector noise coefficients as weighting parameters. The inclusion of collisional narrowing and cross-coherence in the CARS theory calculations and their effect on best fit temperatures are discussed. These temperatures, measured in a flat-flame burner, are compared with those obtained by Na line-reversal.

I. Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) has received much attention in recent years because of its capability for providing remote *in situ* measurements of major species concentration and temperature with good spatial and temporal resolution in practical combustion environments. The theory and application of CARS are described in a number of recent review articles.¹⁻⁴

The sources of error and noise in CARS thermometry can be broadly classified as instrumental and theoretical or result from perturbations due to the medium being probed. The pulse-to-pulse variation in the spectral energy profile of the broadband dye laser is one source of instrumental noise in multiplex (broadband) CARS. It has been proposed that a spectral dependence of the amplitude fluctuations in the temporal profile of the Stokes laser is an additional source of noise.⁵⁻⁷ An analysis of broadband dye laser noise based on uncorrelated statistically independent modes has been reported.⁸ The authors extend this analysis to nonresonant CARS spectra by assuming uncorrelated pump and Stokes lasers and conclude from their observations that the temporal structure of the multimode lasers makes only a small contribution

to their CARS noise. The CARS signal noise was found to be consistent with the number of dye laser modes contributing to a detector pixel.

There is very little direct experimental evidence comparing the effect of single-mode and multimode pump sources on CARS noise. We have shown previously the use of a single-mode rather than a multimode pump laser leads to a reduction of noise in nonresonant CARS signals down to a level exhibited by the Stokes laser spectral profile itself.⁷ In this paper we extend this comparison to N₂ resonant spectra.

The CARS noise has been measured both by performing single-pulse temperature measurements in a constant temperature source (a flat-flame burner) and, as previously,⁷ by measuring the shot-to-shot variability of the spectral profile. Measurements of the component of this noise attributable to the detector are also presented.

The use of these measured detector noise variances as weighting parameters in a weighted least-squares fit of experimental and theoretical CARS spectra is shown to increase dramatically the precision (standard deviation for repeated single-shot spectra) of single-pulse CARS temperature measurements.

The accuracy of mean temperatures (or alternatively temperatures derived from averaged spectra) is a subject that is receiving increasing attention. Pealat *et al.*⁹ have recently summarized much of the available evidence which indicates that mean CARS temperatures are typically within 50 K of those obtained by other techniques (principally thermocouple measurements). They⁹ found temperature differences of ± 20 K over the range from 300 to 1500 K. Greenhalgh and Porter¹⁰ observed a comparable accuracy over the temperature range from 300 to 1100 K. We compare mean CARS temperature measurements in a hydrogen/air

T. Parameswaran is with Roy Ball Associates. When this work was done all the other authors were with Defence Research Establishment Ottawa, Ottawa, Ontario K1A 0Z4; they are now with National Research Council of Canada, Division of Mechanical Engineering, Ottawa, Ontario K1A 0R6.

Received 17 June 1986.

0003-6935/87/010099-12\$02.00/0.

fuelled flat-flame burner with those obtained by the sodium line-reversal technique. We also examine the effect of various assumptions in the CARS theory on the best fit temperatures. A preliminary account of these results was presented at a recent conference.¹¹

II. Experimental

A. CARS Spectrometer

The optical layout of the CARS spectrometer used for this study is described elsewhere.^{7,12} The 3-D phase matching technique employed involves passing the Stokes beam coaxially through the annular pump beam. Single-longitudinal-mode operation of the Quanta Ray DCR 1A is achieved using the electronic line narrowing (ELN-2) device. The ELN-2 controls the oscillator to maintain a low gain for a time sufficient to achieve a narrow linewidth. The laser is then rapidly Q-switched to provide maximum gain producing a pulse of high spectral purity. With careful adjustment of the Q-switch bias and the intracavity etalon, ~50% of the pulses are single mode and exhibit the smooth temporal profile indicative of the absence of mode beating.

Single-longitudinal-mode (single-mode) data were obtained by using the smooth output signal from the ELN-2 as the spectrometer trigger input on the Tracor Northern TN1710 optical multichannel analyzer (OMA). Multiple-longitudinal-mode (multimode) data were obtained by triggering the OMA from the external timing circuits.

The spectral width of the pump laser was measured with two Fabry-Perot etalons with a 0.27- and 1.7-cm⁻¹ free spectral range, respectively. An unintensified photodiode array was used to display the interference fringes from a single laser pulse.¹³ The measured average spectral widths (FWHM) when operating the laser single mode, multimode with the DCR 1A intracavity etalon, and multimode without the intracavity etalon were 0.016 ± 0.002 cm⁻¹, 0.10 ± 0.03 cm⁻¹, and 0.69 ± 0.05 cm⁻¹, respectively. The single-mode width probably represents the resolution of the 0.27-cm⁻¹ etalon.

To remove the small residual signals remaining on the detector due to image lag, it was necessary to perform two cleansing scans of the detector between each laser pulse.¹⁴ When the detector was read 60 ms after exposure (see Fig. 1), the residual signal (as registered by the first cleansing scan) was determined to be 0.25% of the original signal. No residual signal was detected by the second cleansing scan. The cleansing scans were initiated by the external read signal from the external timing circuits triggering the OMA to read but not store the diode intensities. The laser pulse and signal integration began immediately after completion of the cleansing scans. The entire cycle was completed within 100 ms for 10-Hz operation.

The acquisition and storage of 1024-element spectra at a 10-Hz rate were accomplished through a complex hardware and software interfacing procedure. As each spectrum was collected by the OMA, a previous

Fig. 1. Optical multichannel detector read sequence.

Fig. 2. Average N₂ spectrum with average nonresonant reference above and referenced spectrum below.

one was transferred to the DEC VAX 11/730 where it was checked for saturation or transmission errors. The data were transmitted and temporarily stored in binary form to increase speed and reduce storage. On completion of a collection run, the data were treated by postprocessing software on the VAX. This included multiplication by 8 (to retain accuracy during later manipulation of the data), subtraction of the background spectrum, division by the nonresonant spectrum (to correct for diode-to-diode sensitivity variations and the spectral variations due to the dye laser, spectrometer, etc.), calculation of the average spectrum for the collection, and permanent storage of these treated spectra in binary form (2k bytes/spectrum). A typical multimode unreferenced hot flame spectrum, the associated nonresonant reference, and the referenced spectrum are shown in Fig. 2. Averaged (100–400 pulses) background and nonresonant reference spectra were recorded at the beginning and end of each data acquisition period. These nonresonant CARS spectra were recorded by placing a carbon dioxide filled cell at the focal volume. To provide a sufficient CARS signal the cell was pressurized to 3 atm.

It is necessary to correct the CARS signals by subtracting a background which results from detector dark current, detector fixed pattern noise, and a small signal due to scattered 532-nm radiation. This background signal was obtained by acquiring spectra while blocking the Stokes laser.

The burner in Fig. 3 was designed to have a premixed well-controlled constant-temperature stabilized flat-

Fig. 3. Flat-flame burner construction.

flame.^{15,16} The flame front established itself in a equilibrium position a short distance from the burner surface where the heat loss to the water-cooled burner reduced the flame speed to the mixture stream velocity. The region probed was the flame from the inner combustion zone. The outer combustion zone protects the flame from large temperature gradients. The sheath of inert gas further protects the flame from atmospheric effects. Temperature calibration of the burner was performed using the sodium line-reversal technique.¹⁶ The burner was calibrated for a hydrogen/air flame at an equivalence ratio of 0.574 and CO₂ as the sheath gas. The linear flow velocity was ~30 cm/s. The measured Na line-reversal temperature 10 mm above burner center was 1575 ± 15 K. The precision (day-to-day repeatability) of the line-reversal measurement was typically ± 7 K, and, including estimates for the systematic errors,¹⁶ we conclude that the measurement is accurate to ± 15 K.

III. Theory and CARS Data Reduction

A. Theory

The theory of CARS has been dealt with extensively in Refs. 1–4. In brief, CARS is a nonlinear optical phenomenon involving three-wave mixing. When two laser beams of frequencies ω_p and ω_s interact in a medium, three-wave mixing produces a resultant coherent beam with frequency ω_{as} , and this is the CARS beam. The mixing occurs for all samples, but the CARS signal is greatly enhanced when $\omega_p - \omega_s$ approaches a Raman frequency of the sample medium.

The interaction of the laser radiation with the medium occurs through the third-order nonlinear electric susceptibility denoted by $\chi^{(3)}$. This gives rise to an induced polarization field which acts as the source term in Maxwell's wave equation. On solving the wave equation one gets for monochromatic input waves the intensity of the CARS signal as

$$I(\omega_{as}) \sim I_p^2 I_s |\chi^{(3)}|^2, \quad (1)$$

where I_p , I_s , and $I(\omega_{as})$ represent the pump, Stokes, and

CARS intensities, respectively. $\chi^{(3)}$ has resonant χ^R and nonresonant χ^{NR} contributions.

The nonresonant susceptibility χ^{NR} is real and proportional to the total number density. Raman active modes involved in the CARS spectra of combustion processes are strongly polarized vibration rotation transitions. It is considered sufficiently accurate to restrict calculations to the Q-branch. The widths of these Raman lines are functions of pressure, temperature, and rotational quantum number.¹⁷ When pressure increases the lines broaden and may overlap; at higher pressures, when there is sufficient interference between adjacent transitions, collisional narrowing occurs,^{18,19} and the system relaxes according to the density matrix equation. The resonant susceptibility χ^R for overlapping Raman lines may then be expressed in terms of a G matrix given by²⁰

$$G_{ts} = i(\omega_p - \omega_s - \omega_t)\delta_{ts} + \frac{\Gamma_t}{2}\delta_{ts} + \gamma_{ts}(1 - \delta_{ts}), \quad (2)$$

where ω_p , ω_s , ω_t denote the pump, Stokes, and Raman frequencies, respectively, Γ_t is the isolated linewidth, δ_{ts} is the Kronecker delta symbol, and γ_{ts} are the off-diagonal elements of the relaxation rate G matrix. In Eq. (2), γ_{ts} are assumed to be real, and line shifts are neglected. Koszykowski *et al.*²¹ have shown that by using an eigenvalue eigenvector approach χ^R may be calculated from

$$\chi^R(\delta) = \sum_j \frac{a_j}{\lambda'_j - \delta + i\lambda''_j}, \quad (3)$$

where $\lambda_j = \lambda'_j + i\lambda''_j$ is a complex eigenvalue of the G matrix, δ is the detuning, which should not be confused with the Kronecker delta δ_{ts} , and a_j is in general a complex weight factor. At low pressures one may neglect the overlap between lines and set γ_{ts} to 0; then λ'_j approaches the Raman frequency ω_j ; λ''_j approaches Γ_j , the Raman linewidth; and χ^R reduces to

$$\chi^R(\delta) = \frac{4\pi N c^4}{h \omega_s^4} \sum_j \frac{\Delta\rho_{jj}(d\sigma/d\Omega)_j}{2\delta - i\Gamma_j}. \quad (4)$$

This is the isolated line approximation. The Raman cross section $d\sigma/d\Omega$ can be obtained from Placzek-Teller coefficients and the polarizability parameters for the molecule. $\Delta\rho_{jj}$ refers to the fractional population in the j th state, and N is the number density.

Knowing χ^R and χ^{NR} , Eq. (1) can be directly used to get the CARS spectrum for monochromatic laser beams. The effect of laser bandwidths on theoretical CARS spectra is treated extensively by Yuratich.²² In a standard method widely used in CARS theory, the final CARS intensities are obtained by a simple convolution of $|\chi^{(3)}|^2$ with the pump and Stokes spectral profiles.^{23–25} This approach ignores the cross terms that arise from the coherence between the polarization components in which the roles of the driving and scattered pump photons are exchanged. In this approximation, when the pump width is very small and the Stokes width is much greater, the CARS intensity may be expressed as

$$I(\omega_{as}) \sim I_p \int I_s[\omega_p^{(0)} - \delta] I_p(\omega_{as} - \delta) |\chi^{(3)}(\delta)|^2 d\delta, \quad (5)$$

where $\omega_p^{(0)}$ is the center frequency of the pump. In actual calculations the convolution with the dye profile was eliminated by ratioing experimental CARS spectra with a nonresonant reference spectrum.

A computer program based on Eq. (5) and the isolated line approximation was used to calculate theoretical spectra. A Gaussian spectral shape was assumed for the pump. Storing the pump exponents once calculated and reusing them helped reduce the convolution cpu time. All the computations were done with the DEC VAX 11/730 computer.

The CARS spectrum thus generated was convolved with a Voigt instrumental (slit) function. Since an exact Voigt is rather too complicated, an approximate expression due to Whiting²⁶ was used. This approximation [Eq. (5) of Ref. 26] is expressed in terms of a Voigt width w_V and a Lorentz width w_L related to the Gaussian width w_G as follows:

$$w_V = \frac{w_L}{2} + \left(\frac{w_L^2}{4} + w_G^2 \right)^{1/2}. \quad (6)$$

An asymmetric Voigt with different values of w_V and w_L on the higher and lower cm^{-1} sides was found to be suitable.

Initially the Voigt parameters were obtained from room temperature (RT) CARS spectra of N_2 . Theoretical RT spectra of N_2 were convolved with a Voigt of trial parameters and compared with experimental spectra. Best fit values of w_V and w_L were obtained with a nonlinear least-mean-squares fitting program based on the well-known Gauss-Newton algorithm as adapted by Kim.²⁷

The Voigt function determined from several RT N_2 spectra was used for convolution with theoretical spectra at temperatures ranging from 300 to 2700 K. A fitting program similar to the one used for the slit function calculation was then employed to fit hot theoretical spectra with experimental spectra, and best fit values of temperatures were determined. In this procedure, temperature and frequency shift between theory and experiment were used as fit parameters. It is too time-consuming to generate the theoretical spectra for each iteration, and, therefore, a library of spectra calculated at 50 K intervals was used. These spectra were interpolated for intermediate temperatures.

The flame temperatures thus determined were somewhat sensitive to the Voigt slit parameters. Hence attempts were made to obtain the four Voigt parameters as well as temperature and frequency with a six-parameter fitting scheme. The results of these fits are discussed in a later section.

B. Input Variables

The variables that determine the theoretical CARS spectrum of a molecule are as follows: the spectroscopic constants; the Raman linewidth Γ_j ; the concentration; temperature T ; pressure P ; nonresonant susceptibility χ^{NR} ; the Raman cross section $d\sigma/d\Omega$; the pump laser frequency $\omega_p^{(0)}$ and bandwidth $\Delta\omega_p$; and the

statistical weight factors. The term $d\sigma/d\Omega$ was calculated for every level from the molecular polarizability parameters.²⁸ The spectroscopic constants were obtained from Rahn.²⁹ For the isolated lines the widths were calculated according to Hall.³⁰ There has been considerable uncertainty in the scaling of the χ^{NR} of diatomic molecules. Rosasco and Hurst³¹ and Lundeen *et al.*³² review the various measurements. For N_2 we have used the value of $8.31 \times 10^{-18} \text{ cm}^3/\text{erg}$, which is the average of that quoted by Rosasco and Hurst³¹ and that reported by Farrow.³³ The χ^{NR} values for O_2 and Ar that are needed for the H_2/air flame were taken from Ref. 31. For H_2O the χ^{NR} used was $18.29 \times 10^{-18} \text{ cm}^3/\text{erg}$.³³ Further details of CARS input variables are described in Ref. 34. All the theoretical spectra were generated at 1-atm pressure.

C. Collisional Narrowing

It is now accepted that,²¹ while collisional narrowing of Raman lines cannot be neglected for CARS spectra at high pressures, it can become significant even at atmospheric pressures. To test this effect a library of theoretical spectra with collisional narrowing was also generated. These calculations were based on Eqs. (3) and (5). The off-diagonal line matrix elements γ_{ts} of the relaxation rate matrix were obtained with an exponential gap law²⁰ model.

D. Cross-Coherence Effects

Teets³⁵ and Kataoka *et al.*³⁶ have observed that neglecting the cross-coherence terms that arise in the laser convolution of CARS intensities can lead to temperature errors, especially when the pump bandwidth is comparable to the Raman linewidth and the nonresonant contribution competes with the resonant signal. Including this effect, the CARS intensity may be written (not including dye convolution) as

$$I_{as}(\omega_{as}) = \chi_{NR}^2 \langle 1 \rangle + 2\chi_{NR} \langle \text{Re} \chi_R(\omega_{as} - \omega') \rangle + \frac{1}{2} \langle |\chi_R(\omega_{as} - \omega')|^2 \rangle + \frac{1}{2} \langle \chi_R(\omega_{as} - \omega') \chi_R(\omega_{as} - \omega'') \rangle, \quad (7)$$

where

$$\langle F \rangle = \int d\omega' I_p(\omega') \int d\omega'' I_p(\omega'') F(\omega', \omega''). \quad (8)$$

Normally the fourth term in Eq. (7) is difficult to evaluate because of the double integral. However, analytical closed form expressions for this problem have been derived by Teets³⁵ for a Lorentzian pump profile and by Greenhalgh and Hall³⁷ for Gaussian pumps. For the latter case the fourth term $I^{(cc)}$ may be given in terms of an error function $w(Z_j)$:

$$I_{as}^{(cc)}(\omega_{as}) = \frac{\Pi}{2\Delta\omega_p^2} \left| \sum_j a_j w_j(Z_j) \right|^2, \quad (9)$$

where cc refers to cross-coherence, $\Delta\omega_p$ is the pump width, and Z_j is a complex argument given below:

$$Z_j = \frac{-[\lambda_j' - [\omega_{as} - \omega_p^{(0)}]] - i\lambda_j''}{\Delta\omega_p}. \quad (10)$$

We have included this term in the CARS program with the collisional narrowing corrections. The complex error functions were generated with an efficient algorithm by Hui *et al.*³⁸ With this technique the cross-coherence terms did not require large amounts of computer time.

Results obtained from the three theoretical models (isolated line approximation, collisional narrowing, and the latter with accurate laser convolution including cross-coherence effects) will be compared to experimental CARS spectra in a later section.

IV. Results and Discussion

A. Detector Noise and Absolute Sensitivity

To compare detector performance at constant sensitivity we measured the absolute sensitivity of three Tracor Northern intensified diode array detectors (IDARSS), an older TN-1223-4GI, and two newer TN-6132s. A calibrated irradiance standard was used to illuminate the diodes directly. The radiation was isolated to a 60-nm band centered at 507 nm, and the IDARSS exposure was calculated by integrating the product of the lamp spectral irradiance and the filter transmission over the bandpass of the filter. Neutral density filters were used to limit further the exposure to $1.02 \times 10^{-3} \mu\text{W}/\text{cm}^2$, which, for a 0.02-s exposure, corresponds to $1.3 \times 10^{-4} \text{ J/diode}$ or 3.2×10^4 photons/diode at 507 nm.

The absolute sensitivities obtained were: for the two TN-6132 detectors, 2.9 and 3.5 photons/count at a video amplifier setting of $\times 4$ and 9.5 and 11.5 photons/count at a video amplifier setting of $\times 1$; and for the TN-1223-4GI detector, 1.3 photons/count. (We consistently observed the video amplifiers of the TN-6132 detectors to have a gain of ~ 3.4 .)

Detector noise was measured in two ways. First, under conditions of constant illumination, a set of (typically 100) spectra was acquired, and the mean and standard deviation was calculated diode by diode. An average of these diode by diode standard deviations then gave a single noise figure for the detector. Second, a set of spectra was recorded where each spectrum resulted from acquiring two spectra, the first of which was added to, and the second of which was subtracted from, the spectral data memory. The noise (standard deviation) was $\sqrt{2}$ higher using the second method as would be expected from two statistically uncorrelated processes. The second method was preferred for measuring detector noise as a function of light level, since it placed fewer demands on the constancy of the light source.

The noise (a single standard deviation expressed as a percentage of the signal counts) is shown in Fig. 4 as a function of the light level for two different detectors. Controlling the detector is the Tracor Northern 1710, which provides a front panel control of intensifier gain over a range of ~ 100 , and this was used to vary the overall sensitivity of the detector. The detector shot noise shows the $E^{-1/2}$ dependence expected of a process which obeys Poisson statistics. At very high in-

Fig. 4. Detector shot noise as a function of incident light intensity.

Fig. 5. Detector shot noise as a function of signal counts for a fixed intensifier setting.

tensities, the noise falls off less rapidly than this as dark current noise and fixed pattern diode read noise become important. For an ideal detector exposed to a signal of E quanta the standard deviation associated with the signal is $E^{1/2}$. The ideal detector curve is shown in Fig. 4 where the $\sqrt{2}$ factor results from using the second method to obtain the noise statistics. The measured noise of the two detectors is between 1.5 and $2.0\times$ this quantum limit.

The data in Fig. 4 were recorded over a range of intensifier settings. The measured signal variance as a function of signal counts at a fixed intensifier setting is shown in Fig. 5. The measured variance was linear in signal counts as expected, and the intercept corresponded to the measured detector dark noise. The noise was measured in this way for a range of intensifier settings to obtain the coefficients σ_0 and k in the expression

$$\sigma^2 = \sigma_0^2 + kC. \quad (11)$$

σ_0 was largely independent of intensifier setting but k increased with increasing sensitivity. These parameters were used to calculate the weighting coefficients used in the least-mean-squares fitting routines described below.

B. Noise in CARS Spectra

Temperatures are derived from the shape of CARS spectra. Thus one source of noise is the pulse-to-pulse

variability in the spectral energy profile of the dye laser. We have used the method described previously⁷ to measure the shot-to-shot variability of the CARS spectral profile. The analysis procedure is outlined below.

A set of CARS spectra can be represented by S_{ij} where

$$S_{ij} = I_{ij}K_i, \\ i = 1 \dots N \text{ diodes,} \\ j = 1 \dots N \text{ pulses,} \quad (12)$$

with i representing the diode number of the diode array detector and j the spectrum index. I_{ij} is the CARS intensity associated with the diode number i and spectrum number j , and K_i is the sensitivity of diode i . The individual spectra are divided by an average spectrum to produce a ratioed CARS signal X_{ij} where

$$X_{ij} = (S_{ij}/\bar{S}_i) = \left(I_{ij} / \sum_j I_{ij} \right) M. \quad (13)$$

The ratioed CARS signal is now independent of diode sensitivity and represents the shot-to-shot variation of the CARS spectral profile from an averaged spectrum.

Finally, if N_L and N_U are the lower and upper diode limits for the spectral region of interest, the normalized CARS signal Y_{ij} is given by

$$Y_{ij} = X_{ij} / \sum_{i=N_L}^{N_U} X_{ij}. \quad (14)$$

The standard deviation of each spectrum Y_{ij} about the mean yields a percentage noise N_j , which, when averaged over the M spectra, gives an average noise $\bar{N}$ and a standard deviation σ , which represents the shot-to-shot variability of the noise.

From a detailed analysis of nonresonant CARS spectra we have shown previously⁷ that when a single-mode pump laser is used, the CARS noise is reduced to a level exhibited by the Stokes laser itself ($\sim 5\%$ noise at 2.0-cm^{-1} resolution and 70-cm^{-1} bandwidth for our broadband dye laser).

We have repeated the earlier nonresonant analysis and have also included the analysis of resonant flame N_2 spectra recorded in the flat-flame burner. The spectra were digitized at a 0.25-cm^{-1} interval, and a 15-cm^{-1} spectral region was analyzed. The nonresonant spectra were recorded at a low detector sensitivity where the effect of detector shot noise is negligible. The resonant noise can be corrected for the residual detector shot noise by assuming that the detector shot noise σ_D and the noise in signal σ_C are uncorrelated giving a net noise σ_N :

$$\sigma_N^2 = \sigma_C^2 + \sigma_D^2. \quad (15)$$

This corrected noise σ_C , attributable to pulse-to-pulse variations in the spectral profile of the CARS signal, is shown in parentheses in Table I.

The results confirm the earlier conclusion⁷ that the nonresonant spectra recorded with a single-mode

Table I. Noise statistics: Standard Deviation σ Expressed as Percent

Spectrum type	Pump Laser Configuration		
	Single mode	Multimode (0.10 cm^{-1})	Multimode (0.69 cm^{-1})
CO ₂ nonresonant spectra	6.6	8.4	9.1
N ₂ flame spectra $T = 1580\text{ K}$	22.4 (22.0)	16.1 (15.6)	11.1 (10.8)

pump laser exhibit less noise than those recorded with a multimode pump laser. The actual noise values are somewhat higher than we observed previously, and we speculate on the cause of this below. For the resonant spectra the reverse is true, and the single-mode spectra exhibit greater noise, with the noise decreasing with an increasing multimode laser bandwidth.

This noise, expressed as a percentage, was largely constant and thus represents a fixed fraction of the total signal. Thus the total noise σ_T associated with a particular diode count C can be expressed as

$$\sigma_T^2 = \sigma_0^2 + kC + mC^2, \quad (16)$$

where σ_0^2 is the dark noise or noise in the absence of a signal, kC is the shot noise component, and mC^2 represents the component associated with the shot-to-shot variation in the CARS signals. The mC^2 term is an approximation in that m is difficult to measure, and the percentage noise in signal probably increases at very low signal levels.

In a weighted least-squares fit the parameters are determined by minimizing the weighted sum of squares where the reciprocal of the variance is used as the weighting coefficient. The above expression for σ_T has been used to perform a weighted least-squares fit of experimental CARS data, as described below.

C. Single-Shot CARS Temperature Measurements

Single-shot CARS temperature measurements were performed in the hydrogen/air fueled flat-flame burner with single-mode and multimode pump laser operation. Typically sets of 100 spectra were recorded and the spectra analyzed individually. The data collection system automatically averages the individual spectra, and these average spectra were also analyzed. Mean temperature and standard deviation were calculated for each set of individual spectra, and the results were averaged.

One aim of these experiments was to examine whether the greater noise of single-mode resonant spectra, shown in Table I, would be reflected in a bigger temperature spread in the single-shot data. Typical results are shown in Fig. 6. The widths of histograms in Fig. 6 represent the instrumental resolution, since no temperature variations are expected in the premixed flame. It can be seen that, as expected from the above analysis of spectral shapes, the single-mode histograms are significantly wider than the multimode ones. This confirms the conclusion that resonant CARS spectra, unlike nonresonant spectra,

Fig. 6. Temperature histograms calculated for single-mode and multimode (0.1-cm⁻¹) pump operation with weighted and unweighted least-mean-squares fits using isolated line computer program.

exhibit greater noise with a single-mode pump laser than with multimode pump laser.

We also performed a weighted least-mean-squares fit of theoretical T and experimental E CARS spectra where the quantity minimized was

$$\sum_i w_i (T_i - E_i)^2, \quad (17)$$

where i is the diode index, and the weighting parameter w_i is $1/\sigma_i^2$. σ_i was calculated from Eq. (17) using experimentally determined values of σ_0 and k and an estimated value of m corresponding to 4% shot-to-shot CARS noise, approximately the noise observed in the Stokes laser.⁷

The effect of weighting the data is to reduce greatly the width of the histograms. The greater than twofold reduction in the width of single-mode temperature histograms is particularly dramatic. Thus taking proper account of signal variance can greatly increase the precision of single-pulse CARS measurements.

The histograms in Fig. 6 were calculated using the isolated line approximation. More recently, we included collisional narrowing and cross-coherence effects in the CARS theory code and repeated the earlier isolated line analysis. Essentially the same reductions in standard deviation were obtained when these effects were included, as demonstrated in Tables II, III, and IV. In addition it can be seen from a comparison of Tables III and IV that increasing the spectral width of the multimode pump laser from 0.10 to 0.69 cm⁻¹ results in a reduction in standard deviation. Weighting reduces the standard deviation to ~3% of the average temperature for the larger spectral bandwidth. The effect of the choices of weighting coefficients on the average temperatures and average standard deviations obtained from all the single-pulse data is also

shown in Tables II, III, and IV. The standard deviations are largely insensitive to the amount of CARS noise included in the weighting coefficients. However, a larger CARS noise contribution resulted in a greater temperature shift.

While preparing this manuscript, we learned of similar results obtained by Barton and Garneau.³⁹ They observed standard deviations of 75 K multimode (no intracavity etalon), 91 K (multimode with intracavity etalon), and 102 K (ELN operating but no single-mode conditional sampling) for a 2100 K flame. These trends are consistent with our observations.

Greenhalgh and Porter¹⁰ have reported a dependence of standard deviation on a CARS signal level. We have collected the data in Tables II–IV at approximately constant CARS intensity to minimize such potential effects. In separate experiments we have subsequently investigated the effect of a fivefold reduction in CARS intensity. The standard deviations observed were 70.2 ± 4.0 and 72.4 ± 4.8 K (for a 0.69-cm⁻¹ pump) at normal and reduced CARS intensity, respectively. Thus, unlike Greenhalgh and Porter,¹⁰ we observe no dependence of standard deviation on a CARS signal level. This result is not surprising since the average detector shot noise only increases from ~2 to ~4% with decreasing CARS signal and is substantially less than the measured noise-in-signal (Table I).

The cause of the systematic temperature shifts with weighting is not clear. However, it should be noted that the weighted fits are more sensitive to the value of the nonresonant susceptibility (χ^{NR}) used in calculation of the theoretical spectra. We have examined the effect of changing χ^{NR} by 10% on the best fit temperatures with weighting (4% CARS noise) and without. The fit to the single-mode data (including collisional

Table II. Effect of Weighting Coefficients on Analysis of Single-Pulse Single-Mode Data with Collisional Narrowing Included in CARS Theory

Average temperature $\bar{T}_{av}$ (K)	Standard deviation $\bar{\sigma}_T$ (K)	Weighting
1563	131 ± 17	None
1551	71 ± 5	Detector shot noise only
1531	59 ± 6	Detector shot noise +4% CARS noise
1492	61 ± 7	Detector shot noise +20% CARS noise

Note: Error limits are 95% confidence intervals.

Table III. Effect of Weighting Coefficients on Analysis of Single-pulse multimode (0.10-cm⁻¹) Pump Laser Data with Collisional Narrowing and Cross-Coherence Included in CARS Theory

Average temperature $\bar{T}_{av}$ (K)	Standard deviation $\bar{\sigma}_T$ (K)	Weighting
1586	88 ± 5	None
1554	51 ± 3	Detector shot noise only
1526	45 ± 2	Detector shot noise +4% CARS noise

Note: Error limits are 95% confidence intervals.

Table IV. Effect of Weighting Coefficients on Analysis of Single-Pulse Multimode (0.69-cm⁻¹) Pump Laser Data with Collisional Narrowing and Cross-Coherence Included in CARS Theory

Average temperature $\bar{T}_{av}$ (K)	Standard deviation $\bar{\sigma}_T$ (K)	Weighting
1602	71 ± 6	None
1555	46 ± 4	Detector shot noise only
1532	42 ± 5	Detector shot noise +4% CARS noise

Note: Error limits are 95% confidence intervals.

narrowing) produced temperature changes of 9 K (unweighted fit) and 18 K (weighted fit). The corresponding numbers for the 0.1-cm⁻¹ multimode data (with the effect of cross-coherence included) were 13 and 24 K. A decrease in χ^{NR} leads to an increase in the fitted temperatures. Thus a 20% decrease in the value of χ^{NR} used would eliminate about one-half of the single-pulse temperature shifts observed in Tables II and III and would entirely eliminate the similar but smaller shifts observed in fitting the multipulse averaged spectra.

Another possibility is that, although care was taken to avoid nonlinear behavior of the diode array detec-

tor,¹² some small residual effect remained. If so, the weighted best fit temperatures would be expected to be lower because of their greater emphasis on the lower intensity portion of the spectrum.

The selection of weighting coefficients appears to be a compromise between reducing the standard deviation and avoiding temperature shifts. Weighting places emphasis on the lower intensity parts of the CARS spectrum and thus the need, for example, to know χ^{NR} (and hence composition) accurately. The nonresonant background can be eliminated [with an accompanying large (sixteen fold) reduction in CARS signal]. However, unspecified temperature shifts have been observed in fitting background-free spectra.⁹ Weighting with terms associated with detector noise only is sufficient to realize most of the reduction in standard deviation while minimizing the temperature shifts.

Pealat *et al.*⁹ have also performed weighted fits of experiment to theory. On the basis of an analysis of Poisson noise they minimized

$$\sum_i T_i (\ln E_i - \ln T_i)^2,$$

where the theoretical intensities T_i were used as weighting parameters. They did not compare weighted and unweighted fits. Their weighting scheme is equivalent to a linear fit with a weighting coefficient of $1/T_i$ and would thus be expected to have a similar effect to weighting with $\sigma_0 = m = 0$ in Eq. (16). They note that, if the T_i weighting is neglected in their fits, a temperature bias results. Since this latter weighting scheme would be equivalent to setting $\sigma_0 = k = 0$ in Eq. (16) and retaining only the CARS noise term, this is consistent with our observation of temperature shifts with larger values of m . It should be noted that the presence of the σ_0 term in Eq. (16) limits the emphasis put on the very low intensity portion of the CARS spectrum.

The use of a multimode laser clearly confers an advantage in reducing the single-shot CARS noise and thus reducing the temperature spreads observed with repeated single-shot temperature measurements. With this advantage comes the greater complexity of the CARS theory calculations, although the recently developed analytic solutions^{35,37} of the cross-coherence effects minimize this difficulty. The possible effect of pump laser field statistics on the ratio of the resonant to nonresonant CARS signal^{40,41} is a problem which can be avoided by using a single-mode pump laser. For some lasers, the ratio of nonresonant to resonant CARS signal is found to increase^{40,41} with increasing correlation between the pump laser components. If such increases occurred in our experiments, they would require use of an artificially high value of χ_{NR} to fit the spectra, which, as noted above, would increase the discrepancy between the weighted and unweighted fits. Furthermore, any increase in χ_{NR} would lower the best-fit multimode temperatures in Table V that are already at the lower limits of agree-

Table V. Summary of Multipulse CARS Temperature Measurements 10 mm above Burner Center

Temperature (K)	Computer model
Single-mode pump laser	
1577 ± 17	Isolated line
1599 ± 19	Collisional narrowing
Multimode (0.10-cm ⁻¹) pump laser	
1588 ± 10	Isolated line
1611 ± 11	Collisional narrowing
1569 ± 11	Collisional narrowing + cross-coherence
Multimode (0.69-cm ⁻¹) pump laser	
1659 ± 7	Isolated line
1581 ± 7	Collisional narrowing + cross-coherence

Note: Error limits are 95% confidence intervals.

ment with both the single-mode pump laser temperatures and the Na line-reversal temperatures.

A quantitative evaluation of the reduction of CARS noise with increasing pump laser bandwidth does not appear possible in the present state of the emerging theories of CARS noise. We have attempted to model this process by computing the quantity

$$\frac{\sigma}{\langle I \rangle} = \left[\sum_k \langle I_k \rangle^2 \right]^{1/2} / \sum_k \langle I_k \rangle,$$

which represents the noise attributable to k -independent modes of intensity I_k .⁸ σ is the standard deviation, and the $\langle \rangle$ brackets indicate a time average. We have taken the Stokes laser mode spacing to be 0.01 cm⁻¹ (approximately the lowest-order TEM₀₀ mode spacing), and I_k was calculated as the pump convolved CARS intensity at the 0.01-cm⁻¹ interval. The summation was performed over all the I_k values falling under the envelope of the Voigt instrument function, and the ratio $\sigma/\langle I \rangle$ was calculated as a function of frequency (cm⁻¹) for pump laser widths (FWHM) of 0.69, 0.1, and 0.016 cm⁻¹ (approximately single-mode conditions). The theoretical noise spectra exhibited peaks which coincided with the peaks in the CARS spectrum, and the noise increased with decreasing pump laser bandwidth. The average noise in the 1–0 band was ~17% (0.016 cm⁻¹), 12.5% (0.10 cm⁻¹), and 6.2% (0.69 cm⁻¹), where the pump laser bandwidths are in parentheses. The noise, calculated in a similar way, for a purely nonresonant spectrum was 5.6% independent of pump laser bandwidth.

The experimental noise figures in Table I show a similar trend with pump laser bandwidth, but the absolute values are somewhat higher. The experimental resonant noise spectra also exhibited peaks which coincided with those of the CARS spectrum itself, but, unlike the theoretical noise spectra, they did not exhibit the falloff of noise in the region of the 2–1 band and beyond (21,060–21,100 cm⁻¹). This may be due to the increasing importance of uncorrected detector shot noise in these low-intensity portions of the CARS spectrum.

Nonresonant experimental spectra demonstrate increasing noise with increasing laser bandwidth (Table I), a fact not predicted by the calculations discussed above. This may be attributable to amplitude fluctuations in the temporal profile of the Stokes laser, which increase with increasing pump laser bandwidth.⁷

These amplitude fluctuations⁷ were invoked^{5–7} to explain the increase in noise observed when a multimode pump laser (rather than the temporally smooth single-mode pump laser) was used to pump the Stokes laser and excite the nonresonant CARS spectra. The amplitude fluctuations in our system⁷ appear to result from the Stokes laser attempting to follow the temporal behavior of the pump laser.

In summary, the observed behavior can be viewed as resulting from (spectral) averaging over a greater number of Stokes laser modes as the bandwidth of the pump laser increases. This beneficial averaging is offset by an increase in noise due to an increase in the amplitude fluctuations of the Stokes laser with increasing pump laser bandwidth. The spectral averaging will be particularly important in the flame spectra where very few Stokes modes contribute to the excitation of the narrow (0.03–0.04-cm⁻¹) Raman resonances when a single-mode pump laser is used. In this regard the dual-broadband CARS approach of Eckbreth and Anderson⁴² should, as noted by the authors, result in reduced noise because of the use of two statistically independent dye sources, which should reduce both sources of noise discussed above.

At lower temperatures or higher pressures the beneficial averaging resulting from the larger pump laser bandwidth would be expected to decrease because of the increased Raman linewidths. As the Raman linewidths increase the noise behavior observed with nonresonant CARS spectra should be approached.

D. Multipulse Average CARS Temperature Measurements

The question of the accuracy of the flat-flame burner CARS temperature measurements and their dependence on including collisional narrowing and cross-coherence effects in the CARS theory is more readily addressed by analyzing multipulse averaged CARS spectra. The true mean temperature should be equal to the temperature obtained from an average spectrum for an isothermal source such as our flat-flame burner.

A 100-pulse average single-mode CARS flame spectrum and a best-fit theory spectrum calculated with collisional narrowing effects included in the CARS code are shown in Fig. 7. The spectrum was recorded 10 mm above the burner surface on the center line. The estimated sodium line-reversal temperature 10 mm above the burner surface was 1593 ± 18 K. CARS temperature measurements taken along the Na line-reversal axis showed that the center line temperature was some 18 K hotter than the average temperature observed over the Na seeded region of the flame. Thus the observed sodium line-reversal temperature of 1575 ± 15 K was increased by this amount to give the estimated center line value of 1593 ± 18 K.

Fig. 7. Experimental single-mode N_2 CARS flame spectrum compared with a best fit theory spectrum calculated with collisional narrowing included.

Over a period of six months we recorded a series of multimode and single-mode 100–400-pulse average CARS spectra 10 mm above burner center. The data were initially analyzed using the isolated line approximation for the Raman lines and later by including the effects of collisional narrowing and cross-coherence. We have also examined the consistency of the instrumental (slit) function by determining the four Voigt parameters from both room temperature and flame spectra. The room temperature instrument function was routinely used to obtain the temperatures reported here. The average temperatures so obtained are summarized in Table V. Including collisional narrowing increases the best-fit temperatures of single-mode and the 0.1-cm⁻¹ multimode pump laser data by 20–25 K, and the final temperature derived from the single-mode data is in excellent agreement with the Na line-reversal temperature. With collisional narrowing included, the instrument (slit) functions determined from either single-mode room temperature or flame N_2 spectra were essentially identical. With the isolated line model the room temperature slit function was 10–15% narrower than that derived from hot spectra.

With multimode data cross-coherence must also be included in the calculations, and as shown in Table V the effect is to lower the best fit temperatures ~40 K. Collisional narrowing and cross-coherence have opposing effects on best-fit temperatures, and the final temperature is only 19 K less than the isolated line temperature. This cancellation is a function of the assumed pump bandwidth since an attempt to fit to the data with an assumed 0.4-cm⁻¹ pump laser bandwidth (the laser manufacturer's specification) produced a final best fit temperature of 1531 K, some 57 K lower than the isolated line temperature and 62 K lower than the Na line-reversal temperature. The 0.1-cm⁻¹ pump laser result of 1569 ± 11 K is in satisfactory agreement with the Na line-reversal temperature of 1593 ± 18 K. The instrument function was very similar to that derived from the single-mode data.

The effect of neglecting collisional narrowing and cross-coherence is much more marked for the 0.69-

cm⁻¹ multimode data. The isolated line best fit temperature of 1659 K is in poor agreement with the sodium line-reversal temperature and with the single-mode temperatures. With collisional narrowing and cross-coherence effects included in the code, the best-fit temperature of 1581 is in excellent agreement with the Na line-reversal temperature of 1593 K.

Reducing χ^{NR} by 20% gives approximate best fit temperatures of 1617 ± 19 K (single-mode) and 1595 ± 11 K (multimode 0.10 cm⁻¹) in equally good agreement with the line-reversal temperature of 1593 ± 18 K.

We conclude that it is necessary to include the effects of collisional narrowing and cross-coherence to predict correctly CARS temperatures in atmospheric pressure flames. With these effects included the calculated temperatures are within 25 K of the Na line-reversal temperatures for both multimode and single-mode pump laser data.

E. Stokes Laser Noise

With the large number of modes excited in the Stokes laser there is the possibility⁶ of selective focusing of these modes whereby the lower-order modes may focus more tightly and thus more efficiently wave mix with the pump laser field. In our earlier work we saw no evidence of this, but the astigmatism produced by a tilted CARS focusing lens may have masked any effect.

As noted above the observed nonresonant noise (8.0% with a 70-cm⁻¹ analysis bandwidth) with a single-mode pump laser was higher than that observed previously⁷ (5.7%). We, therefore, investigated the effect of adding a beam expansion telescope to the Stokes laser with a magnification of 1.0, with lenses chosen to deliberately induce some spherical aberration. With this arrangement the CARS intensity dropped a factor of ~2, and the observed nonresonant noise was 5.5%. When the telescope was removed the noise returned to the previous 8.0%.

The 5.5% noise is approximately equal to the 5% noise previously observed in the Stokes laser itself.⁷ A plausible explanation of this observation is that the spherical aberration introduced in the Stokes laser blurred any tendency for selective focusing of various modes. Thus the pump laser wave mixed with a Stokes laser whose modes were effectively spatially averaged.

V. Conclusions

From an analysis of both the shot-to-shot variation in spectral shape of CARS spectra and the standard deviation of the temperatures calculated from them, we conclude that increasing the pump laser spectral bandwidth decreases the CARS noise. The use of a multimode pump laser is clearly indicated for the generation of low-noise resonant spectra at low to moderate pressures.

The precision of the single-pulse temperature measurements can be dramatically increased by performing weighted fits of theoretical and experimental CARS spectra. The weighting coefficients were de-

rived from experimental measurements of detector noise and noise in the CARS signal itself.

To obtain accurate temperature measurements in atmospheric pressure flames, it is necessary to include collisional narrowing (for both single-mode and multimode) and cross-coherence (multimode only) effects in the CARS theory. With the appropriate effects included, both the single-mode and multimode pump laser data gave flame temperatures which agreed with Na line-reversal to better than 25 K at 1600 K.

The authors would like to acknowledge the help provided by the United Technologies Research Center (UTRC) in supplying a copy of the original isolated line program. T. Parameswaran would like to thank R. J. Hall of UTRC for continued help and advice on the development of the computer programs needed for generating the theoretical CARS spectra.

The authors would also like to acknowledge the help of F. D. Findlay for participation in the sodium line-reversal measurements and contributions to development of CARS spectroscopy at DREO.

References

1. S. A. J. Druet and J. P. E. Taran, "CARS Spectroscopy," *Prog. Quantum Electron.* **7**, 1 (1981).
2. R. J. Hall and A. C. Eckbreth, "Coherent Anti-Stokes Raman Spectroscopy (CARS): Application to Combustion Diagnostics," in *Laser Applications*, Vol. 5, J. F. Ready and R. K. Erf, Eds. (Academic, New York, 1984), pp. 213-309.
3. A. B. Harvey, Ed., *Chemical Applications of Nonlinear Raman Spectroscopy* (Academic, New York, 1981).
4. J. W. Nibler and G. V. Knighten, "Coherent Anti-Stokes Raman Spectroscopy," in *Raman Spectroscopy of Gases and Liquids*, A. Weber, Ed. (Springer, Berlin, 1979), pp. 253-299.
5. A. C. Eckbreth, G. M. Dobbs, J. H. Stufflebeam, and P. A. Tellex, "CARS Temperature and Species Measurements in Augmented Jet Engine Exhausts," *Appl. Opt.* **23**, 1328 (1984).
6. A. C. Eckbreth and J. H. Stufflebeam, "Considerations for the Application of CARS to Turbulent Reacting Flows," *Exp. Fluids* **3**, 301 (1985).
7. D. R. Snelling, R. A. Sawchuk, and R. E. Mueller, "Single-Pulse CARS Noise: A Comparison Between Single-Mode and Multimode Pump Lasers," *Appl. Opt.* **24**, 2771 (1985).
8. D. A. Greenhalgh and S. T. Whittle, "Mode Noise in Broadband CARS Spectroscopy," *Appl. Opt.* **24**, 907 (1985).
9. M. Pealat, P. Bourchard, M. Lefebvre, and J. P. Taran, "Precision of Multiplex CARS Temperature Measurements," *Appl. Opt.* **24**, 1012 (1985).
10. D. A. Greenhalgh and F. M. Porter, "CARS Applications in Chemical Reactors, Combustion and Heat Transfer," in *Proceedings, First International Laser Sciences Conference*, Dallas (Nov. 1985).
11. D. R. Snelling, G. J. Smallwood, R. A. Sawchuk, and T. Parameswaran, "Nonlinearity and Single Shot Noise Problems in CARS Spectroscopy," at Sixty-seventh AGARD PEP Meeting on Advanced Instrumentation for Aeroengine Components, Philadelphia (May 1986).
12. D. R. Snelling, R. A. Sawchuk, and G. J. Smallwood, "Multichannel Light Detectors and Their Use for CARS Spectroscopy," *Appl. Opt.* **23**, 4083 (1984).
13. M. B. Morris and T. J. McIlrath, "Portable High-Resolution Laser Monochromator-Interferometer with Multichannel Electronic Readout," *Appl. Opt.* **18**, 4145 (1979).
14. L. P. Goss, D. D. Trump, B. G. MacDonald, and G. L. Switzer, "10 Hz Coherent Anti-Stokes Raman Spectroscopy Apparatus for Turbulent Combustion Studies," *Rev. Sci. Instrum.* **54**, 563 (1983).
15. J. P. Botha, and D. B. Spalding, "The Laminar Flame Speed of Propane/Air Mixtures with Heat Extraction from the Flame," *Proc. R. Soc. London Ser. A* **225**, 71 (1954).
16. D. R. Snelling and M. Fischer, "Design and Calibration of a Flat-Flame Burner using Line-Reversal Techniques," Technical Note 85-4, Defence Research Establishment Ottawa, Canada (1985).
17. F. Printer, "Dependence of the Width of the Rotational Raman Lines of N_2 and CO_2 on the Quantum Number j ," *Opt. Spectrosc. USSR* **17**, 428 (1964).
18. A. D. May, J. C. Stryland, and G. Varghese, "Collisional Narrowing of the Vibrational Raman Band of Nitrogen and Carbon Monoxide," *Can. J. Phys.* **48**, 2331 (1970).
19. J. Bonamy, L. Bonamy, and D. Robert, "Overlapping Effects and Motional Narrowing in Molecular Band Shapes: Application to the Q-Branch of HD," *J. Chem. Phys.* **67**, 4441 (1977).
20. R. J. Hall, "Coherent Anti-Stokes Modelling for Combustion Diagnostics," *Opt. Eng.* **22**, 322 (1983).
21. M. L. Koszykowski, R. L. Farrow, and R. E. Palmer, "Calculation of Collisionally Narrowed Coherent Anti-Stokes Raman Spectroscopy Spectra," *Opt. Lett.* **10**, 478 (1985).
22. M. A. Yuratich, "Effect of Laser Linewidth on Coherent Anti-Stokes Raman Spectroscopy," *Mol. Phys.* **38**, 625 (1979).
23. R. J. Hall, "CARS Spectra of Combustion Gases," *Combust. Flame* **35**, 77 (1979).
24. R. L. Farrow, P. L. Mattern, and L. A. Rahn, "Comparison Between CARS and Corrected Thermocouple Temperature Measurements in a Diffusion Flame," *Appl. Opt.* **21**, 3119 (1982).
25. T. Lasser, "An Alternative Method for CARS Spectra Convolutions," *Opt. Commun.* **35**, 447 (1980).
26. E. E. Whiting, "An Empirical Approximation to the Voigt Function," *J. Quant. Spectrosc. Radiat. Transfer* **8**, 1379 (1968).
27. H. Kim, "Computer Programming in Physical Chemistry Laboratory," *J. Chem. Educ.* **2**, 120 (1970).
28. C. M. Penney, R. L. St. Peters, and M. Lapp, "Absolute Rotational Raman Cross Sections for N_2 , O_2 , and CO_2 ," *J. Opt. Soc. Am.* **64**, 712 (1974).
29. L. A. Rahn, Sandia National Laboratories, unpublished results.
30. R. J. Hall, "Pressure Broadened Linewidths for CARS Thermometry," *Appl. Spectrosc.* **34**, 780 (1980).
31. G. J. Rosasco and W. S. Hurst, "Measurement of Resonant and Nonresonant Third Order Nonlinear Susceptibilities by Coherent Raman Spectroscopy," *Phys. Rev. A* **32**, 281 (1985).
32. T. Lundeen, S. Y. Hou, and J. W. Nibler, "Nonresonant Third Order Susceptibilities of Various Gases," *J. Chem. Phys.* **79**, 6301 (1983).
33. R. L. Farrow, Sandia Laboratories, Livermore, CA; private communication.
34. T. Parameswaran and D. R. Snelling, "A Computer Program to Generate Coherent Anti-Stokes Raman Spectra," Technical Note 81-18, Defence Research Establishment Ottawa, Canada (1982).
35. R. E. Teets, "Accurate Convolutions of Coherent Anti-Stokes Raman Spectra," *Opt. Lett.* **9**, 226 (1984).
36. H. Kataoka, S. Maeda, and C. Hirose, "Effects of Laser Line Width on the Coherent Anti-Stokes Raman Spectroscopy Spectral Profile," *Appl. Spectrosc.* **36**, 565 (1982).
37. D. A. Greenhalgh and R. J. Hall, "A Closed Form Solution for the CARS Intensity Convolution," *Opt. Commun.* **57**, 125 (1986).
38. A. K. Hui, B. H. Armstrong, and A. A. Wray, "Rapid Computation of the Voigt and Complex Error Functions," *J. Quant.*

Spectrosc. Radiat. Transfer 19, 509 (1978).

39. S. A. Barton and J. M. Garneau, Defence Research Establishment Valcartier, Quebec City; private communication.
40. L. A. Rahn, R. L. Farrow, and R. P. Lucht, "Effects of Laser Field Statistics on Coherent Anti-Stokes Raman Spectroscopy Intensities," Opt. Lett. 9, 223 (1984).
41. R. L. Farrow, L. A. Rahn, and R. P. Lucht, "Effect of Non-

Gaussian Pump Fuels Statistics on Unresolved CARS Spectra," in *Proceedings, Ninth International Conference on Raman Spectroscopy* (Chemical Society of Japan, Tokyo, 1984), pp. 340-341.

42. A. C. Eckbreth and T. J. Anderson, "Dual Broadband CARS for Simultaneous Multiple Species Measurements," App. Opt. 24, 2731 (1985).

Meetings continued from page 90

1987 April

- 13-17 Laser Safety: Hazards, Inspection & Control course, San Francisco *Laser Inst. of Amer., 5151 Monroe St., Toledo, OH 43623*
- 14-17 Antenna Analysis, Design, & Measurements course, Tempe *Ctr. for Professional Development, Coll. of Eng. & Applied Sciences, AZ State U., Tempe, AZ 85287*
- 20-24 Fundamentals & Applications of Lasers course, San Francisco *Laser Inst. of Amer., 5151 Monroe St., Toledo, OH 43623*
- 27-1 May Conf. Lasers & Electro-Optics, Baltimore *OSA Mtgs. Dept., 1816 Jefferson Pl., N.W., Wash., DC 20036*
- 27-1 May Int. Quantum Electronics Conf., Baltimore *OSA Mtgs. Dept., 1816 Jefferson Pl., N.W., Wash., DC 20036*
- 28-30 Fiber Optics course, London *Sira Ltd., South Hill, Chislehurst, Kent BR7 5EH, UK*
- 30 Optical Micro Metrology of Surfaces Mtg., London *D. Swift, Pilkington P E Ltd., Glascoed Rd., St. Asaph, Clwyd, LL17 0LL, UK*

May

- 4-7 Advanced Industrial Laser Safety Officers course, San Francisco *Laser Inst. of Amer., 5151 Monroe St., Toledo, OH 43623*
- 11 Intro. to Acoustic Emission for Nondestructive Testing course, Norman *D. Egle, 865 Asp Ave., Rm. 212, Oklahoma U., Norman, OK 73019*
- 11-15 Applied Optics course, Las Cruces *L. Radziemski, Physics Dept., NMSU, Las Cruces, NM 88003*
- 11-15 SID'87, New Orleans *M. Goldfarb, Palisades Inst. for Res. Services Inc., 201 Varick St., New York, NY 10014*
- 12-15 Int. Symp. on Optical Particle Sizing: Theory and Practice, Rouen *G. Gouesbet, Dept. Chem. Eng., INSA de Rouen, BP08, 76130 Mont-Saint-Aignan, France*
- 13-15 7th Int. Workshop on Expert Systems & Their Applications, Avignon *Agence de l'Informatique, Tour Fiat, 92084 Paris-La Defense, Cedex 16, France*
- 17-22 40th Ann. SPSE Conf. & Symp. on Hybrid Imaging Systems, Rochester *D. Wilkalis, P.O. Box 821, Fairport, NY 14550*

18-20 SIAM Conf. on Optimization, Houston *Soc. for Industrial & Applied Mathematics, 14th Fl., 117 S. 17th St., Phila., PA 19103*

18-21 Modern Experimental Spectroscopy course, Las Cruces *Laser Inst. of Amer., 5151 Monroe St., Toledo, OH 43623*

27-29 6th Int. IPAT Mtg., Brighton *D. Cowan, Tech. Media Services, 62 Kelvingrove St., Glasgow G3 7SA, UK*

June

- 15-28 The Effects of Modes of Formation on the Structure of Glass Conf., Nashville *D. Kinser, Box 1689-B, Vanderbilt U., Nashville, TN 37235*
- 15-29 Disordered Solids: Structures & Processes course, Erice, Italy *B. Di Bartolo, Dept. Physics, Boston Coll., Chestnut Hill, MA 02167*
- 17-25 21st Session of the Int. Commission on Illumination, Venice *W. Budde, NRC, Ottawa, Canada KIA 0R6*
- 21-25 5th National Synchrotron Radiation Instrumentation Conf., Madison *R. Ward, Synchrotron Radiation Ctr., 3725 Schneider Dr., Stoughton, WI 53589*
- 22-26 Laser Mtg., Munich *Kallman Assoc., 5 Maple Ct., Ridgewood, NJ 07450*
- 22-26 Optical Image Processing & Pattern Recognition course, Madison *F. Drake, Eng. Professional Development Dept., U. WI, 432 N. Lake St., Madison, WI 53706*
- 22-26 8th Int. Conf. on Laser Spectroscopy, Åre *S. Svanberg, Box 118, S-221 00 Lund, Sweden*
- 29-30 Color Appearance Top. Mtg., Annapolis *OSA Mtgs. Dept., 1816 Jefferson Pl., N.W., Wash., DC 20036*

July

- 1-3 Color Vision Deficiencies Int. Symp., Annapolis *B. Drum, Johns Hopkins U., School of Medicine, Wilmer Ophthalmological Inst., 601 N. Broadway B-27, Baltimore, MD 21205*
- 1-4 Computer Assisted Radiology Mtg., Berlin *IEEE, 345 E. 47th St., New York, NY 10017*

continued on page 113