

Intensities in pure rotational CARS of air^{a)}

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(Received 10 November 1979; accepted 27 December 1979)

Measurements of the pure rotational CARS spectrum of N₂ and O₂ in air are reported. The spectrum was obtained using a three-color pulsed laser arrangement. Quantitative agreement between experiment and the calculated variations in intensity and line shape is obtained.

I. INTRODUCTION

Coherent antisokes Raman spectroscopy (CARS) presents a number of aspects such as high sensitivity, high spectral resolution, or the ability to study extremely small volumes of matter that make it an attractive spectroscopic tool. In recent reviews of this technique,^{1,2} these features have been discussed, together with the basic theory and experimental arrangement. A CARS signal is generated when a sample is irradiated with two or three high power laser beams. In the region where the light beams with frequencies ω_1 , ω_2 , and ω_3 overlap (in space and time), radiation is produced with frequency $\omega_4 = \omega_1 + \omega_2 - \omega_3$. Because the process is coherent, the emitted beam is highly directional with wave vector $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$. This enhances detectability relative to incoherent processes such as ordinary or hyper Raman scattering, especially if the orientation of \mathbf{k}_4 differs from the orientations of the other three (incident) propagation vectors. Because of the difficulty in obtaining satisfactory (and reproducible) overlap of several highly focused, high-power pulsed lasers, a three-color experiment is simpler to implement than the four-color case. Thus, in "conventional" CARS, two lasers are used as sources so that $\omega_1 \equiv \omega_2$ and $\mathbf{k}_4 = 2\mathbf{k}_1 - \mathbf{k}_3$. When one (or both) of these lasers is tuned, a strong signal is generated when $\omega_1 - \omega_3 = \omega_r$, where ω_r is a Raman frequency of the medium. The necessity of using a dye laser as one of the light sources has for the most part limited this type of CARS experiment to measurements of frequency shifts ω_r of at least a few hundred wave numbers. At frequency shifts lower than this, $\mathbf{k}_1 - \mathbf{k}_3$ and the spatial separation between the generated beam and the incident beams is insufficient to keep the superradiance from the dye laser from masking the weaker CARS signal. This superradiance arises when fluorescence in the dye propagates along the active lasing region and thereby stimulates intense, broadband emission that is collinear with the incident light. While careful alignment of the lasers and spatial filtering will minimize the superradiance, it cannot be entirely eliminated in this fashion.

While hydrogen-containing molecules H_nX, where X is H or a heavy atom, have rotational Raman spacings large enough to give ω_r that enable one to bypass this problem³ (particularly for high-*J* transitions), pure ro-

tational CARS spectra of heavy molecules have been obtained only with recourse to alternative experimental arrangements. Beattie *et al.*⁴ have used the four-color CARS approach mentioned above to obtain the pure rotational CARS spectrum of air. The BOXCAR technique⁵ employed by Goss and Harvey⁶ is a modification of the four-color experiment in which the high frequency input beam is split into two that are focused into the sample from different directions. This gives three incident wave vectors (but only two frequencies), with the result that \mathbf{k}_4 , the wave vector of the generated beam, can be quite different from any of \mathbf{k}_1 , \mathbf{k}_2 , \mathbf{k}_3 even when $\omega_4 \approx \omega_1$ (and $\omega_2 \equiv \omega_1 \approx \omega_3$). In addition to the increased experimental problems in focusing three beams into the scattering volume, the conversion efficiency will be lower in a cross-beam configuration due to reduction in the overlap volume of the beams.

In this paper we report measurements of the pure rotational CARS spectrum of air made with a conventional apparatus using relatively low power dye lasers (~20 kW at the sample). The key to surmounting the superradiance problem is in performing a depolarized experiment. When the incident beams are orthogonally polarized, the CARS radiation is polarized parallel to the Stokes (lower frequency) laser.⁷ For a collinear beam geometry, the ratio of this depolarized intensity to the CARS intensity resulting from parallel-polarized incident beams is given by the square of the corresponding spontaneous Raman depolarization ratio.⁷ For a rotational line, the CARS ratio has the value 9/16. Consequently there is little loss in sensitivity in performing a depolarized rotational CARS experiment rather than the polarized equivalent.

One of the features of this CARS experiment is that intensities of many rotational lines can be measured. One not only has the opportunity to study the reproducibility of such data, but one can determine how the observed line shapes and intensities vary with changes in the incident laser light. Finally, one can attempt to fit these data to theoretical expressions which are based on well-known equations for the spontaneous Raman intensities for pure rotational transitions.

II. EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1. For collinear incident beams with orthogonal polarizations, the CARS signal is polarized perpendicular to the high frequency or pump beam⁷ and is essentially collinear with the input beams. Thus, insertion

^{a)}This work supported by a research grant from the National Science Foundation; the equipment was purchased with the aid of a Departmental Instrumentation grant from the National Science Foundation.

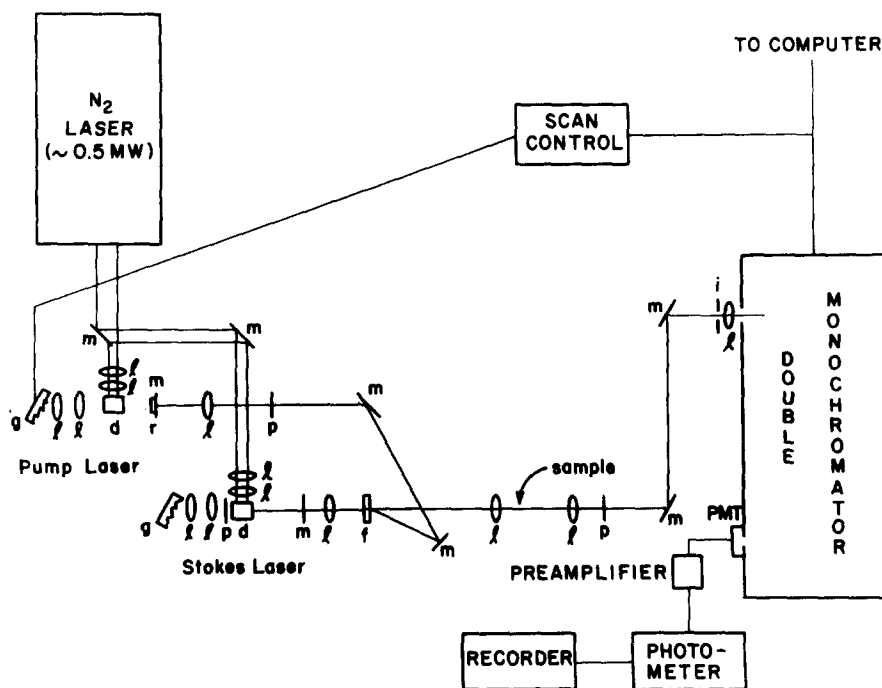


FIG. 1. Low frequency CARS arrangement. The dye lasers are pumped by a Moletron nitrogen laser. Code: l, lens; m, mirror; d, dye cell; p, polarizing filter; r, rochon polarizing crystal; i, iris; PMT, photomultiplier tube; g, grating; f, interference filter.

of a polarizing filter will block the pump beam and its accompanying superradiance. Because of the absence of spatial separation, it is necessary to use a monochromator to separate the intensity at ω_4 from that at ω_1 and ω_3 . Of course, if one can eliminate the intense pump beam at ω_1 with a polarizer, the detection problem is simplified, especially in view of the fact that ω_4 is closer to ω_1 than to the unfiltered Stokes beam with frequency ω_3 . In these experiments, the pump laser and the monochromator are scanned in tandem while the Stokes laser frequency is held fixed. Superradiance from the Stokes laser can thus be reduced with a narrow-band interference filter. Evidently, the limitations to measuring generated beam intensities at very small frequency shifts are determined by the width of the pass band of the interference filter and by the ability of the monochromator to discriminate against the remnant laser light. Using an inexpensive filter (Corion #16998) with a FWHM = 10 Å and a peak transmission of 54%, we could detect down to the N_2 $J = 4 \rightarrow J = 6$ transition in air at 1 atm, a Raman shift of ~ 44 cm^{-1} . The monochromator served here as an additional variable frequency filter and thus was operated using relatively large slit openings. Computer control was used to ensure that the monochromator was driven at twice the scan rate of the dye laser frequency.

The interference filter, having a reflectivity of over 95%, is also used to efficiently combine the laser beams (dichroic mirrors of course being less useful for small CARS shift experiments). The ~ 0.5 nsec temporal mismatch of the laser pulses resulting from the increased path length traversed by the pump laser is not a serious loss for the 6 nsec pulses. However, etaloning from the interference filter causes a variation in the light intensity incident on the sample. As seen from the nonresonant CARS generated from glass (Fig. 2), this produces

$\sim 10\%$ uncertainty in the spectral intensities. The regularity of this etalon effect allows one to correct for these variations; this is necessary only in very high precision measurements and was not attempted in the present work.

The low-frequency depolarized CARS spectrum of air is displayed in Fig. 3. Due to the broadness of the interference filter's pass band, some superradiance from the Stokes laser reaches the detector. Subtraction of the smoothly varying background yields the rotational CARS spectrum displayed in Fig. 4. The frequency shifts of these lines are given quite accurately by the usual Raman expression

$$\omega_r(J) = B_v(4J+6) - 4D_v(2J+3)(J^2 + 3J + 3), \quad (1)$$

with^{8,9}

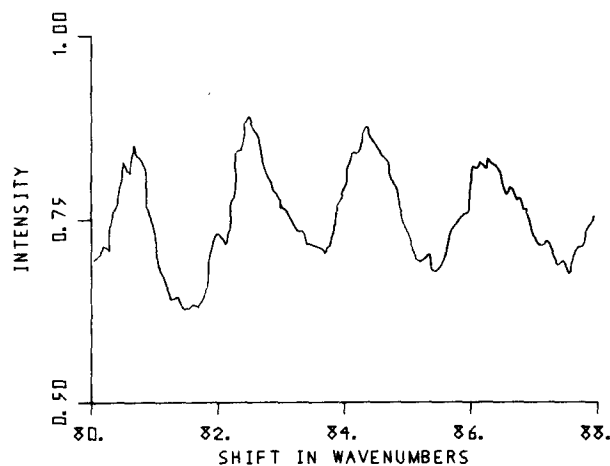


FIG. 2. Nonresonant CARS from glass. Spectral intensities in this and subsequent figures are in arbitrary units; frequencies are Raman shifts.

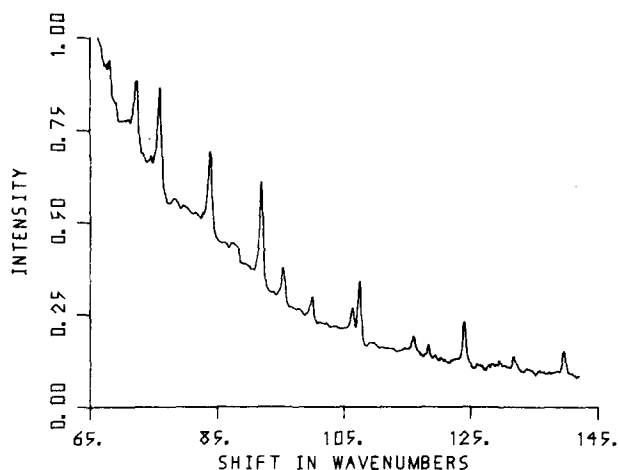


FIG. 3. Low frequency CARS spectrum. Background intensity is superradiance from the Stokes laser.

$$B_0 = 1.9896 \text{ cm}^{-1}, \quad D_0 = 5.76 \times 10^{-6} \text{ cm}^{-1}(\text{N}_2),$$

$$B_0 = 1.4376 \text{ cm}^{-1}, \quad D_0 = 4.81 \times 10^{-6} \text{ cm}^{-1}(\text{O}_2).$$

A comparison between experimental and theoretical intensity variations over the spectrum is a more challenging exercise. The usual expressions for CARS intensity¹⁰ are valid in the case of a Lorentzian line in the spontaneous Raman which is excited by laser beams with linewidths negligibly small compared to the width of the Raman transition. The reverse situation occurs in these experiments: the widths of the pure rotational spontaneous Raman lines for gas at 1 atm are small compared to the laser linewidths. Furthermore, our lasers exhibit Gaussian intensity profiles¹¹ rather than Lorentzian. If one adapts the results obtained by Yuratich in a recent study of the effects of laser line width on CARS spectra,¹² one can write $I_{\text{CARS}}(\omega)$, the intensity of the CARS spectrum detected at frequency $\omega_{\text{as}} = \omega_1 + \omega$ with $\omega = \omega_1 - \omega_3$, as

$$I_{\text{CARS}}(\omega) \propto \left| \sum_{i,J} [I(\omega)]_{i,J} + iB \right|^2 \quad (2)$$

for a series of transitions due to the change in rotational quantum state of a molecule of species i from quantum number J to $J+2$. The electronic background susceptibility B is included for generality; it is negligible in a pure rotational experiment, since the resonant signal arises from the permanent anisotropy in the polarizability (in vibrational CARS, where the nuclear motion merely induces an anisotropy in the polarizability, the signal is much weaker relative to the electronic background and the nonresonant term can be of sufficient relative magnitude to severely distort the shape of the spectrum).¹¹ The quantity $[I(\omega)]_{i,J}$ is

$$[I(\omega)]_{i,J} = N_i \Delta_{i,J} \left(\frac{d\sigma}{d\Omega} \right)_{i,J} F(\omega), \quad (3)$$

where $F(\omega)$ is the laser line shape function, $\Delta_{i,J}$ is the line strength factor times the difference in state population of states J and $J+2$ for a molecule of species i ,¹ N_i is the total number of molecules of species i in the scattering volume, and $(d\sigma/d\Omega)_{i,J}$ is determined by the

spontaneous Raman cross section. It is well known that¹³

$$\left(\frac{d\sigma}{d\Omega} \right)_{i,J} = \sigma_{i,J} \beta_i^2 (2J+1) / Q_i, \quad (4)$$

where $\sigma_{i,J}$ is the nuclear spin weight (2/3 or 1/3 for N_2 when J is even or odd, respectively; 0 and 1 for O_2 when J is even or odd). The quantity β_i is the polarizability anisotropy and Q_i is the rotational partition function, for species i . One also has

$$\Delta_{i,J} = S(J) \{ \exp[-E_i(J)/kT] - \exp[-E_i(J+2)/kT] \}, \quad (5)$$

where the line strength factor for linear molecules in $^1\Sigma$ states is

$$S(J) = \frac{(J+1)(J+2)}{(2J+1)(2J+3)}, \quad (6)$$

and the rotational energy for species i in its vibrational ground state is

$$E_i(J) = (B_0)_i J(J+1) - (D_0)_i J^2(J+1)^2. \quad (7)$$

Equation (3) is valid only when the intrinsic linewidths of the spectral transitions (of order of 10^{-2} cm^{-1}) is small compared to the incident laser linewidths. Since Yuratich indicates that one should convolute the spectral densities of the two incident beams, and since these spectral densities are both Gaussian, the line shape function $F(\omega)$ can be obtained from the complex Fourier transform of the product of a pair of time-correlation functions for Gaussian spectral densities:

$$F(\omega) = \int_0^\infty e^{-a^2 t^2} e^{i\omega t} dt, \quad (8)$$

where $a^2 = a_p^2 + a_s^2$, with the parameter a^2 (for the pump and Stokes beams) equal to $\omega_{1/2}^2 / 4 \ln 2$, with $\omega_{1/2}$ equal to the HWHM for the incident beam profile. Theoretical spectra were calculated using a fitted value of a equal to $2.3 \times 10^{10} \text{ sec}^{-1}$; experimentally, the HWHM of the pump and Stokes beams were comparable and were estimated to be $0.15 \pm 0.05 \text{ cm}^{-1}$, which would yield $a = 2.4 \times 10^{10} \text{ sec}^{-1}$.

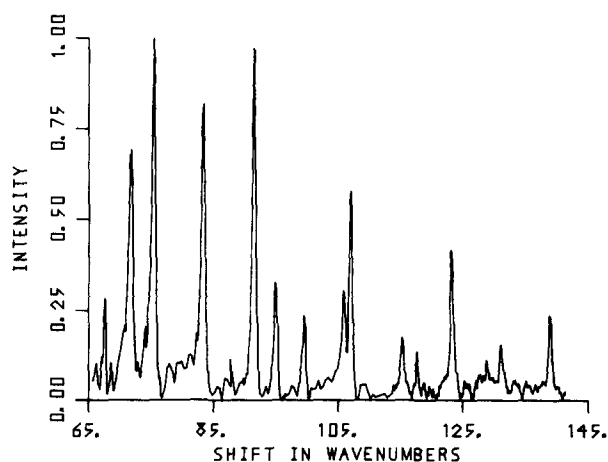


FIG. 4. Experimental pure rotational CARS of air covering the range from $J=7$ to $J=16$ for N_2 (O_2 lines run from $J=11-21$).

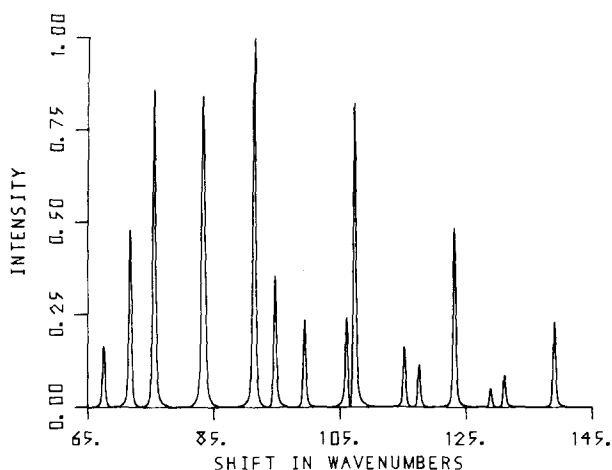


FIG. 5. Calculated pure rotational CARS of air.

Since no absolute intensity measurements were attempted, it is the relative intensity variations with J and with species i that are of interest. If one uses $\beta_{N_2}^2/\beta_{O_2}^2 = 0.57$ (literature value = 0.56),^{14,15} together with the mole fractions for these gases in air, the relative intensities of the N_2 and O_2 spectra are reproduced satisfactorily. A complete theoretical CARS spectrum calculated using Eqs. (2)–(8) is shown in Fig. 5. It is evident that the variations in line strength agree quite well with the experimental observations shown in Fig. 4.

Figure 6 shows the transitions associated with $J=6$ for N_2 and $J=9$ for O_2 on an expanded scale. This pair of lines is routinely resolvable despite the fact that the transition frequencies differ by less than 0.7 cm^{-1} . Two somewhat different spectra are shown; the differences are due to day-to-day variations in incident laser frequency and linewidth; the latter can be nicely accounted for by varying the value of a used in $F(\omega)$.

III. DISCUSSION

The chief goal of this study was to learn if one could make measurements of relative spectral CARS intensity which would be both reproducible and in agreement with theory. Thus, the system chosen was one where the theory could be used for quantitative predictions. It was shown that the experimental peak heights and shapes were accurately proportional to the expected results. We have noted previously that frequency scanning is accompanied by a regular variation of $\sim\sqrt{10}\%$ in the pump laser power reflected from the front surface of the interference filter. This etaloning can also produce a day to day variation of $\sim 10\%$ in the observed intensity of a spectral line. This could be eliminated if the non-scanning Stokes laser were operated at the same wavelength each day and if the angle at which the pump laser strikes the filter surface were kept constant. However, since the free spectral range of the filter is $\sim 2 \text{ cm}^{-1}$, the Stokes laser wavelength must be held fixed to considerably better than $\pm 0.3 \text{ \AA}$, which is not practical with our equipment.

The primary factor affecting precision during a given

experimental session is fluctuations in the CARS signal from shot to shot of the input lasers. These arise not only from fluctuations in the laser output, but from changes in the overlap of the incident beams in the region of sample where the signal is generated (due to thermal lensing and refractive index fluctuations). In a low pressure experiment such as this, averaging over 30 laser pulses is sufficient to reduce the mean square shot-to-shot fluctuation to a few percent. Thus, the experiments were generally run at 10 shots/sec, with signal accumulation over 3 sec. In this way, continuous frequency scanning at rates as fast as $2 \text{ cm}^{-1}/\text{min}$ was feasible while still maintaining satisfactorily high resolution.

The major potential source for error in the intensities is in tracking errors in the monochromator and laser frequency scans. This problem is magnified as one attempts to minimize superradiance by closing the monochromator slits. In practice, it was necessary to reset the tracking drives after a scan of $\sim 30 \text{ cm}^{-1}$; this was done by halting the laser frequency scan, maximizing the nonresonant CARS signal generated when the sample was replaced by a piece of glass, and then restarting the laser scan at a point which would give some overlap between segments of spectrum obtained before and after the adjustment of the monochromator.

One feature of CARS intensities that complicates intensity analysis is that the heights of neighboring lines depends strongly upon the linewidths of the lasers used. This point is illustrated in Fig. 6, where the N_2 line at 59.7 cm^{-1} and the O_2 line at 60.3 cm^{-1} are made to overlap because of convolution of the laser line shapes with the (narrow) intrinsic rotational lines. Because of the coherent nature of this technique, the calculation of these compound line shapes is significantly different from ordinary Raman—note that the “intensity” $I(\omega)$ in Eq. (1) is complex, and that it is summed before squaring. Among other things, this means that interference between radiation generated from different molecules at different points in the illuminated volume has a signifi-

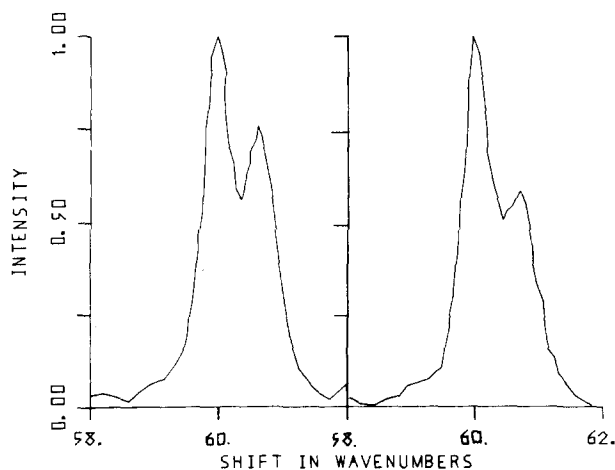


FIG. 6. Expanded view of atmospheric rotational CARS lines for $J=6 \rightarrow J=8$ transition in N_2 and $J=9 \rightarrow J=11$ transition in O_2 .

cant effect on the CARS intensity, independent of correlation (or lack of it) between molecular positions and orientations.

After all sources of error are considered, it is estimated that the line shapes and relative intensities are reproducible to $\sim 10\%$. Agreement between experiment and the theoretical spectrum shown in Fig. 5 was at least as close as this error limit.

This method for obtaining low-frequency CARS spectra is generally applicable to any resonance with an appreciable anisotropic polarizability component. Interference filters with bandpasses of a few angstroms and transmissions greater than 50% are readily available. Alternatively, a highly transmitting, broadband filter could be used in conjunction with an etalon, whose free spectral range exceeds the filter's width. In this manner Raman shifts down to $\sim 15\text{ cm}^{-1}$ should be measurable.

The potential applications of low-frequency CARS include the study of rotational dynamics in dense fluids, collision broadening of rotational lines in gases, low-frequency vibrational modes, and the determination of rotational temperatures.

ACKNOWLEDGMENTS

The authors express their gratitude to Professor Gerd Rosenblatt and David Drapcho for helpful suggestions

and the design of the monochromator scanning program. Dr. David Wright contributed heavily to the early stages of setting up and detecting CARS signals.

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