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RESEARCH AND DEVELOPMENT BRANCH
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DRLO TECHNICAL NOTE 81-18

A COMPUTER PROGRAM TO GENERATE THEORETICAL COHERENT ANTI-STOKES RAMAN SPECTRA

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T. Parameswaran and D.R. Snelling

PROJECT NO. 25B

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Energy Systems Section
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ABSTRACT

A computer code for generating and plotting theoretical CARS (Coherent Anti-Stokes Raman Spectroscopy) spectra is described. This code, which was obtained from Dr. A.C. Eckbreth of the United Technologies Research Centre, was modified for use on a Sigma-9 computer. The theory and computational procedure involved in generating CARS spectra is discussed and the input parameters and variables used in the code are described.

Theoretical nitrogen spectra, which are presented for a range of experimental conditions are discussed.

RESUME

Description d'un code machine permettant de créer et de représenter graphiquement des spectres théoriques obtenus par la spectroscopie Raman "Anti-Stokes" cohérente. Ce code a été fourni par le Dr. A.C. Eckbreth du United Technologies Research Centre et a été modifié pour permettre son emploi avec l'ordinateur Sigma-9. Il y a aussi la description de la théorie et de la procédure de calcul qui entrent dans la création de ces spectres, ainsi que des paramètres et des variables d'entrée employés dans ce code.

On y trouve enfin la représentation des spectres théoriques de l'azote présentés pour toute une gamme de conditions expérimentales.

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ACKNOWLEDGEMENTS

The authors are greatly indebted to Dr. A.C. Eckbreth and Dr. R.J. Hall for supplying their computer code and providing advice on its implementation and use.

INTRODUCTION

A project to develop Coherent Anti-Stokes Raman Spectroscopy (CARS) as a combustion diagnostic tool was recently initiated at DREO. This technique promises to provide the capability of non-perturbing measurements of temperature, pressure, and composition (major species) in real combustion environments. CARS can provide good spatial (<1 mm^3) and temporal (<10 ns) resolution in high interference environments (such as sooting flames which are highly luminescent).

In order to determine the temperature and composition, experimental spectra are fitted to those derived theoretically. Therefore, concurrently with the development of the CARS apparatus, we are undertaking development of the theory and software necessary for the generation of CARS spectra. This work, in part, is being undertaken by Roy Ball Associates Ltd. under contract 2-ST81-000055.

We have been greatly aided by having a computer code, developed by Dr. A.C. Eckbreth's group at United Technologies Research Centre (UTRC), made available to us.

This code was developed by R.J. Hall at UTRC(1,2) on the UNIVAC 1110 Computer. We have suitably modified the above program so that it can be run on the Sigma-9 computer at CRC/DREO. The plots of the resulting spectra are obtained by the additional use of PLOT-10 software with the 4015-1 Tektronix Display terminal. In this note we will explain the theoretical principles underlying this computer program and then discuss some of the procedural details of the Fortran code.

THEORY

The theory of coherent anti-stokes Raman spectroscopy has been dealt with extensively (3,7). In brief, CARS is a nonlinear optical phenomenon and involves three wave mixing. When two laser beams of frequencies ω_ℓ and ω_s interact in a medium, three wave mixing produces a resultant coherent beam with the frequency $2\omega_\ell - \omega_s$ and this is the CARS beam. The mixing occurs for all samples but the intensity of the CARS signal is greatly enhanced when $\omega_\ell - \omega_s$ approaches a Raman frequency of the medium.

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

$$P_3 \propto P_\ell^2 P_s \left| \chi^{(3)} \right|^2 \qquad (1)$$

Thus the CARS power P_3 varies linearly with the Stokes power P_s, quadratically with the pump power P_ℓ and is also proportional to the square of the third order susceptibility. $\chi^{(3)}$ has resonant and non-resonant contributions.

$$\chi^{(3)} = \chi^{R} + \chi^{NR} \tag{2}$$

$\chi^{(R)}$ can be obtained semiclassically or quantum mechanically $^{(8)}$ and is given by

$$\chi^{R} = \frac{2Nc^4}{\hbar\ \omega_s^4} \left.\frac{d\sigma}{d\Omega}\right|_j \left[\frac{\omega_j}{\omega_j^2 - (\omega_\ell - \omega_s)^2 - i\ \Gamma_j\ (\omega_\ell - \omega_s)} \right] \tag{3}$$

where N is the number density, ω_j is the Raman frequency, Γ_j is the Raman line width and $d\sigma/d\Omega$ is the scattering cross section. It is clear that χ^R becomes large when

$$\omega_j \approx \omega_\ell - \omega_s \tag{4}$$

If we define the frequency detuning as

$$\Delta\omega = \omega_j - (\omega_\ell - \omega_s) \qquad \text{and if } \Delta\omega/\omega_j << 1 \tag{5}$$

$$\frac{1}{\omega_j - \Delta\omega} \approx \frac{1}{\omega_j} \left(1 + \frac{\Delta\omega}{\omega_j} \right) . \tag{6}$$

Then eqn (3) becomes

$$\chi^{R} = \frac{2Nc^4}{\hbar\omega_s^4} \left.\frac{d\sigma}{d\Omega}\right|_j \left(\frac{1}{2\Delta\omega_j - i\Gamma_j} \right) \tag{7}$$

Let $$K_j = \frac{2Nc^4}{\hbar\omega_s^4} \Delta_j \left.\frac{d\sigma}{d\Omega}\right|_j \Gamma_j^{-1} \tag{8}$$

where Δ_j is the population difference between the upper and lower states of the rotation-vibration transitions with frequency ω_j. Summing over all such ω_j (with $\Delta J = 0, \pm 2$) that lie near $\omega_\ell - \omega_s$

$$\chi^{(3)} = \sum_j \frac{K_j \Gamma_j}{2\Delta\omega_j - i\Gamma_j} \tag{9}$$

The Raman cross section $\frac{d\sigma}{d\Omega}$ can be expressed as follows for the Q branch.

$$\left| \frac{d\sigma}{d\Omega} \right|_Q = \frac{\omega_s{}^4}{c^4} \frac{\hbar}{2M\omega_0} \left[\alpha^2 + \frac{7}{45} b_J^J \gamma^2 \right] \left[v+1 \right] \tag{10}$$

where M is the reduced mass, ω_0 the angular frequency of the molecular oscillator, b_J^J are the Placzek-Teller coefficients, α is the derivative of the mean molecular polarizability with respect to the inter nuclear coordinate and γ the similar derivative of anisotropy and v is the vibrational quantum number of the initial level.

$\chi^{(3)}$ can thus be calculated from equation $^{(9)}$. Then, treating N and χ^{NR} as parameters the CARS power can be obtained at a given temperature T.

In the above analysis the pump frequency ω_ℓ and the Stokes frequency ω_s have been assumed to be ideally monochromatic. In practice the pump laser may have a finite width and a broadband Stokes laser can be used to get multiplex CARS spectra in a single shot. Assuming the modal phases to be uncorrelated, the laser power can be written as

$$P_\ell = \int P_\ell \; (\omega_\ell) \; d\omega_\ell \; ; \; P_s = \int P_s \; (\omega_s) \; ds \tag{11}$$

and the CARS power P_3 (ω) can be obtained by convoluting over the laser widths.

$$P_3 \{\omega\} \sim \int P_\ell\{\omega_\ell\} d\omega_\ell \int P_\ell\{\omega-\delta\} \; P_s\{\omega_\ell-\delta\} \; |\chi\{\delta\}|^2 d\delta \tag{12}$$

Generally, $\Delta\omega_\ell \ll \Delta\omega_s$ and $\Delta\omega_\ell$ is very small. Therefore $P_s\{\omega_\ell-\delta\}$ can be replaced by P_s $\{\omega_\ell{}^{\{0\}} - \delta\}$ and the integral can be simplified to

$$P_3\{\omega\} \sim P_\ell \int P_s \; \{\omega_\ell{}^{(0)} - \delta\} P_\ell \; \{\omega-\delta\} \; | \; \chi|\delta\}|^2 d\delta \tag{13}$$

The computer program developed by R. Hall utilizes the above convolution integral to compute the CARS intensity as a function of frequency. A Gaussian distribution is assumed for the spectral densities $P_\ell(\omega_\ell)$, $P_s(\omega_s)$

$$\text{i.e. } P_\ell \; \{\omega_\ell\} = \exp \left(- \frac{\Delta\omega_\ell}{\text{width}} \right)^2 \tag{14}$$

$$P_s \; \{ \; \omega_s \; \} = \exp \left(- \frac{\Delta\omega_s}{\text{width}} \right)^2 \tag{15}$$

where $\Delta\omega_\ell = \omega - \omega_\ell, \Delta\omega_s = \omega - \omega_s$ and width denotes the laser line width.

The CARS power obtained from equation (12) should be again convolved over the detector slit function, which is usually taken to be triangular. The final CARS power thus found can be compared with experimental data.

GENERATION OF THEORETICAL CARS SPECTRA

ENERGY LEVELS AND RAMAN FREQUENCIES

For a given temperature T, the main program calculates the energy levels and rotational - vibrational frequencies of a diatomic molecule, based on the Boltzmann distribution. For a vibrating rotator the term values are given by (11)

$$T' = \frac{E(v,J)}{hc} = G(v) + F_v(J) \tag{16}$$

where G(v) is the vibrational and $F_v(J)$ the rotational contributions.

$$\begin{aligned} G(v) &= \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 \\ &\quad + \omega_e y_e (v+\tfrac{1}{2})^3 + \omega_e z_e (v+\tfrac{1}{2})^4 \end{aligned} \tag{17}$$

where v is the vibrational quantum number and $\omega_e, \omega_e x_e, \omega_e y_e, \omega_e z_e$ are spectroscopic constants.

$$F_v(J) = B_v J (J+1) - D_v J^2 (J+1)^2 \tag{18}$$

B_v, D_v are found from the Dunham expansion.

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 \tag{19}$$

$$D_v = D_e + \beta_e (v+\tfrac{1}{2}) \tag{20}$$

where again α_e, β_e, γ_e are spectroscopic constants.

Knowing the energy levels E(v,J) the transition frequencies $\omega_{v,J}$ can be canclulated.

The number of molecules in a vibration level of energy E_v is $N_v \propto \exp(-E_v/KT) = \exp(-1.439\, G(v)/KT)$.

Relative to the ground state v=0 the term values are

$$G_o(v) = \omega_e(v) - \omega_e x_e (v^2+v) + \cdots \tag{21}$$

Thus when $\exp(-1.439\ G_o(v)/KT) \approx \exp(-1.439\ \omega_e v/KT)$ (22)

is small the number of electrons in the level is small. When this quantity is $\leqslant 0.01$ the corresending v + 1 is taken as the limit of vibrational levels that contribute significantly to the CARS intensity.

The number of molecules in the rotational level J of a rigid rotator is given by

$$N_J \propto (2J+1)\ e^{-B_v J(J+1)/KT} \tag{23}$$

Since (2J+1) increases linearly with J, N_J goes through a maximum before going to zero.

Setting $\partial N_J/\partial J = 0$ we get $J\max = \sqrt{\frac{KT}{2B_v hc}} - \frac{1}{2}$

for B = 10.44 cm^{-1}, T = 300° K, $N_J \to 0$ around 3.5 times J_{max}. (see Fig. 9 Ref. (11).

Therefore $\sqrt{\frac{KT}{2B_v hc}}$ is used in the program as a criterion for finding the upper limit of the number of rotational states, that contribute to $\chi^{(3)}$.

POPULATION FACTORS

The vibrational partition function is determined in Subroutine QVIB.

$$Q_{vib} = \sum_v \exp(-G(v)/KT) \tag{24}$$

This subroutine also computes the vibrational population factors

$$\frac{\exp(-G(v)/KT)}{Q_{vib}} = N_v/N$$

where N_v is the number of molecules in state v and N is the total number of molecules.

Similarly function QROT computes the rotational partition function

$$Q_{rot} = \sum_J (2J+1) \exp(-F(J)/KT) \tag{25}$$

Subroutine BOLTZ then calculates the combined Boltzmann population factor required in the expression for the susceptibility $\chi^{(3)}$. The population factor $\Delta_{v,J}$ is given by

$$\Delta_{v,J} = \frac{e^{\frac{-hcF^L(J)}{KT}}}{Q_{rot}} \frac{N_v^L}{N} - \frac{e^{\frac{-hc\, F^U(J)}{KT}}}{Q_{rot}} \frac{N_v^U}{N} \qquad (26)$$

where L denotes the lower state and U the upper state.

NUCLEAR STATISTICAL WEIGHT FACTOR

Molecular wave functions are symmetric or antisymmetric under exchange of nuclei. Generally even J functions are symmetric and odd J antisymmetric or vice versa. When the nuclear spin I=0 the symmetric and antisymmetric states never combine and we see missing lines in the Raman rotational spectrum (e.g. O_2). When nuclear spin $\neq 0$ these spatially symmetric and antisymmetric levels combine but with different statistical weights.

Consider $I_1 = I_2 = \frac{1}{2}$
Then total $I = 1, 0$

I = 1→3 spin functions that are symmetric
I = 0→1 spin function that is antisymmetric

Therefore even I spin functions pair with spatially symmetric functions and odd I spin functions pair with spatially antisymmetric functions.

Thus the statistical weight factor is 3 for odd J and 1 for even J if even J states are symmetric and odd J states are antisymmetric, and vice versa. As a second example,

Consider $I_1 = I_2 = 1$
Then $I = 2, 1, 0$

I = 2→5 symmetric spin functions
I = 1→3 antisymmetric spin functions
I = 0→1 symmetric spin function

Again even I states pair with even J (if symmetric) and odd I states pair with odd J (if antisymmetric) and vice versa. For nitrogen even J states are symmetric and odd J states are antisymmetric; therefore the nuclear spin degeneracy factor is

6 for even J
3 for odd J

These nuclear statistical weight factors are used in summing over the various rotational levels.

RAMAN SCATTERING CROSS SECTION

In its present form this program computes the susceptibility for Q branches only. For Q branches the scattering cross section is given by

$$\frac{d\sigma}{d\Omega}\bigg|_Q = \left(\frac{\omega_s}{c}\right)^4 \quad \frac{\hbar}{2M\omega_o}\left(\alpha^2 + \frac{7b_J^J}{45}\gamma^2\right) \{v+1\}$$

described in eqn (9). Knowing the factors in question, dσ/dΩ can be easily found. The Placzek-Teller factors are from ref (10):

$$b_J^J = \frac{J\ (J+1)}{(2J-1)\ (2J+3)}$$

NON-RESONANT SUSCEPTIBILITY χ^{NR}

The non-resonant part of χ is real and proportional to the number density,

i.e. $$\chi^{NR} = N\alpha'$$

where α' is the molecular polarizability. N the number density at temperature T and pressure P is given by

$$P \times \frac{298}{T}\ \chi^{NR} \quad \text{at} \quad \text{NTP}$$

The number density N of a gas in a mixture of gases is given by

$$N = \frac{\chi_{mole} \times \text{pressure} \times 1.013 \times 10^6}{1.38 \times 10^{-16} \times T} \tag{27}$$

where χ_{mole} is the molar fraction of the gas in question. The factor 1.013×10^6 comes from changing atmosphere to dynes/cm^2.

PRESSURE BROADENING OF RAMAN LINES

The CARS code calculates the Raman line width according to the equation

$$\Gamma\ (J) = P.(8T^{-0.71} - 18.6T^{-1.45}J) \tag{28}$$

where T is the temperature, P the pressure, J the rotational quantum number and $\Gamma(J)$ is the line width FWHM in cm^{-1} for $900K \leqslant T \leqslant 2400K$. This value of $\Gamma(J)$ is based on the isolated line approximation.

The parameters in the above equation were obtained by Hall by a least square fit of N_2-Q branch line widths obtained by Owyoung and Rahn(13) with the theoretical line width model predicted by Bonamy and Robert(14).

CORRECTION FOR $\chi^{(3)}$

This program computes the anharmonicity correction and the correction due to centrifugal distortion that contribute to $\chi^{(3)}$.

These are obtained from the vibrational and vibration-rotation matrix elements of the dipole moment operator with anharmonic terms in the potential (15,16).

The anharmonicity correction is obtained from

$$R_1^{\{v\rightarrow v+1\}} = \frac{1}{4}\,\frac{(v+1)^{\frac{1}{2}}\ (4-6(v+1)\,d + 11(v+1))\,b^2}{\frac{1}{4}\ (4-6d + 11b^2)} \qquad (29)$$

where the quantities d,b, will be described in the next section.

The correction due to centrifugal distortion is given by the matrix element, below for Q branches.

$$\begin{aligned} X_1^{v,J\rightarrow v+1,J} &= \left(\frac{v+1}{2}\right)^{\frac{1}{2}} - \left(\frac{v+2}{4}\right) s + \frac{1}{4}\, s - \frac{1}{4}\, (v-1)\, r^2 \\ &\quad - (v+3)r^2 + \frac{1}{2}(v+1)r^2 + \frac{1}{4}(13v + 16)rb \qquad (30) \\ &\quad - \frac{1}{4}\,(13v+10)rb \end{aligned}$$

where $s = 3J\ (J+1)\frac{\gamma^2}{2}\ ;\quad r = J\ (J+1)\gamma^{3/2}$

NUMBERICAL SCHEME AND CONVOLUTION INTEGRALS

Thus far we have discussed only the frequency independent terms of $\chi^{(3)}$. The frequency appears in the denominator of $\chi^{(3)}$ in the detuning factor.

$$2\Delta\omega_j = 2\{\omega_j - \{\omega_\ell - \omega_s\}\}$$

The numerical scheme in the main program selects a frequency range Δ, divides it into a suitable number of discrete intervals, and generates the frequency shifts $(\omega_\ell - \omega_s)$. $\chi^{(3)}$ is then calculated at all these points summing over all the states in the Q branch.

The numerical scheme also divides the chosen frequency range Δ into intervals at which the CARS power $P_3\,(\omega)$ is calculated. $P_3\,(\omega)$ is calculated by numerical evaluation of the convolution integral in eqn. (13).

Simpsons rule for numerical integration according to which

$$\int_{x_0}^{x_{2m}} ydx = y_0 + 4y_1 + 2y_2 + 4y_3 + \dots + y_{2m} \tag{31}$$

for an even number of intervals, is used to evaluate the integral.

Subroutine SLIT uses the same integration rule for convolution over a triangular slit function. The effect of varying the slit width can be studied by calling SLIT several times.

Plots of the CARS spectra computed by the program are obtained with the Tektronix terminal by using PLOT-10 software.

R. Hall has included additional codes to compute corrections to the susceptibility $\chi^{(3)}$ arising from collisional line narrowing (17). This effect becomes significant at high pressures i.e. > 20 atmospheres. We have not used this part of the code as of now. The details of this section will be described in a later note.

DESCRIPTION OF INPUT PARAMETERS AND VARIABLES IN THE COMPUTER CODE

1. WE, XWE, YWE, ZWE
   These are the molecular spectroscopic constants.

2. BE, DE, B1, B2, D1
   are also spectroscopic constants with the following relation with Herzberg's (11) notation.

   B1 → α_e
   B2 → γ_e
   D1 → β_e

3. SNUC1, SNUC2 are the statistical weights for even and odd levels respectively, due to the nuclear spin degeneracy.

4. CONST is the constant term in $\chi^{(3)}$ given by $\frac{1}{M\omega_0}$ where M is the reduced mass and ω_0 the angular frequency of the molecular oscillator.

5. ALPHA, GAMMA are the derivatives with respect to the internuclear distance of the mean molecular polarizability and anisotropy, respectively.

6. AWID, AWIDE, BWID, BWIDE
   are parameters used to find the temperature and rotational quantum number dependent pressure broadened line width WIDTHP(J) (Refer to R. Hall's paper in App. Spcy (12)).

7. T is the mean rotational - vibrational temperature - an input parameter.

8. PRESS is the gas pressure.

9. XMOLE is the molar fraction of the species.

10. CHINR is the nonresonant part of χ and is also an input parameter.

11. OMEGA1, WID1, OMEGA2, WID2
are the pump laser frequency, width, stokes laser frequency and width in that order.

12. NS, WSLIT
are the number of slit functions and the slit widths for those functions.

13. W3MIN, W3MAX
define the limits of the spectral range for calculations of $\chi^{(3)}$.

14. NV is the number of vibrational states
NJ is the number of rotational states.

15. DENSY is the number density.

16. W3PTS+1 is the number of points at which the convoluted CARS power is calculated.

17. A1, A2, GAMM, BA, DA
are needed for finding the anharmonicity correction VCOR and the centrifugal distortion VJCOR to $\chi^{(3)}$ (15, 16). In relation to Bouanich and Brodbeck's article

$$\mathrm{BA} \rightarrow b; \quad \mathrm{DA} \rightarrow d; \quad A_1 \rightarrow a_1; \quad \mathrm{GAM} \rightarrow \gamma$$

$$\gamma = 2\mathrm{BE}/\mathrm{WE} \qquad b = \mathrm{A1}\sqrt{\mathrm{GAMM}/2}$$

$$d = \mathrm{A2}\ \ \mathrm{GAMM}/2$$

18. PTQ (J) are the Placzek-Teller factors.

19. WIDTHP (J) is the temperature and rotational number dependent pressure broadened Raman line width.

20. E(I,J) are the energy levels
LAMQ (I,J) are the transition frequencies for the Q branch.

21. WTEST = LAMQ (I J) - DOMEGA is the frequency detuning factor.

22. WPTS+1 is the number of frequency points for $\chi^{(3)}$ calculation.

23. FREQ (K+1) stores the above Raman frequencies.

24. OMEGA3 (K+1) stores the frequencies defined by W3PTS for convolution integration.

25. POWER (K+1) stores the CARS power at points defined by Freq (K+1).

26. POWER3 (K+1) is the array of CARS power values after convolution over laser line width.

27. POWER4 (K+1) is the similar array after slit convolution.

28. INITT, BINITT, CHECK, DSPLAY, XFRM, YFRM, XTYPE, YTYPE, TINPUT, FINITT are subroutines from PLOT-10 software.

In the original version of the program these plot routines are included in the main section. We have chosen to separate the plotting package. We calculate and store the required arrays and plot them later as required, with the plotting program CARSPLOT consisting of the above PLOT-10 routines.

RESULTS AND DISCUSSION

The computer program described earlier was used to generate the theoretical CARS spectra of nitrogen. These spectra are displayed in Figures 1 through 3.

These spectra were calculated with a pump laser FWHM of 0.8 cm^{-1} and a width of 175 cm^{-1} for the Stokes laser. The values of non-resonant susceptibility, the molecular polarization parameters and the spectroscopic constants of nitrogen used in the input data were the same as those used by R. Hall (1).

Figure 1 depicts the N_2 CARS spectrum at atmospheric pressure and at a temperature of 2100°K. In Fig. 1a the Q-branch spectrum of N_2 for monochromatic incident beams, is shown. The stronger band is the 0-1 fundamental and the weaker one corresponds to the 1-2 hot band. The spectrum is composed of two distinct envelopes with different intensities. For nitrogen, the nuclear spin is 1 and this leads to a statistical weight factor of 6 for the even J rotational levels and a factor of 3 for the odd J levels. Therefore the even J levels have an intensity about four times that of the odd levels and correspond respectively to the strong and weak spectral envelopes.

In Fig. 1b the CARS power after convolution over the finite widths of the laser beams, is shown. Gaussian spectral profiles have been assumed for both the pump and the Stokes lasers.

The resulting CARS power should be convolved once more over the instrumental slit functions before comparing with an experimental CARS signature. The convolved spectrum for a slit function of 1.0 cm^{-1} is shown in Fig. 1c.

The present program can perform this slit convolution (using a triangular slit function) for any chosen number of slit functions. In Figs. 2a through 2c we see the convolved spectra for the slit functions 0.8, 1.0 and 2.7 cm^{-1} respectively. It is clear that 0.8 and 1.0 cm^{-1} yield high resolution spectra while 2.7 cm^{-1} leads to lower resolution. The prominent peak noticed in the hot band of the higher resolution spectra is due to a spectral overlap between a high J, 0 → 1 branch and lower J, 1 → 2 branch.

The effect of temperature on the theoretical CARS spectra is shown in Fig. 3. A low resolution slit width of 2.7 cm^{-1} was chosen for this purpose. Temperatures used were from 1200° - 2400°K in steps of 300°K. The hot band is sensitive to the temperature, and since the rotational structure is not resolved, it can be used for temperature measurement. The $0 \rightarrow 1$ band however is not greatly affected by temperature.

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FIGURE CAPTIONS

Fig. 1. Q-branch theoretical CARS spectrum of N_2 at T = 2100°K, P = 1 atm.

Fig. 1a. CARS spectrum for monochromatic frequencies.

Fig. 1b. The spectrum convoluted over finite laser widths.

Fig. 1c. The spectrum after slit function convolution, slit width - 1.0 cm^{-1}.

Fig. 2. Effect of slit functions; a) 0.8 cm^{-1}
b) 1.0 cm^{-1}
c) 2.7 cm^{-1}

Fig. 3. Variation of N_2 CARS spectrum with temperature slit width = 2.7 cm^{-1}, P = 1 atm.

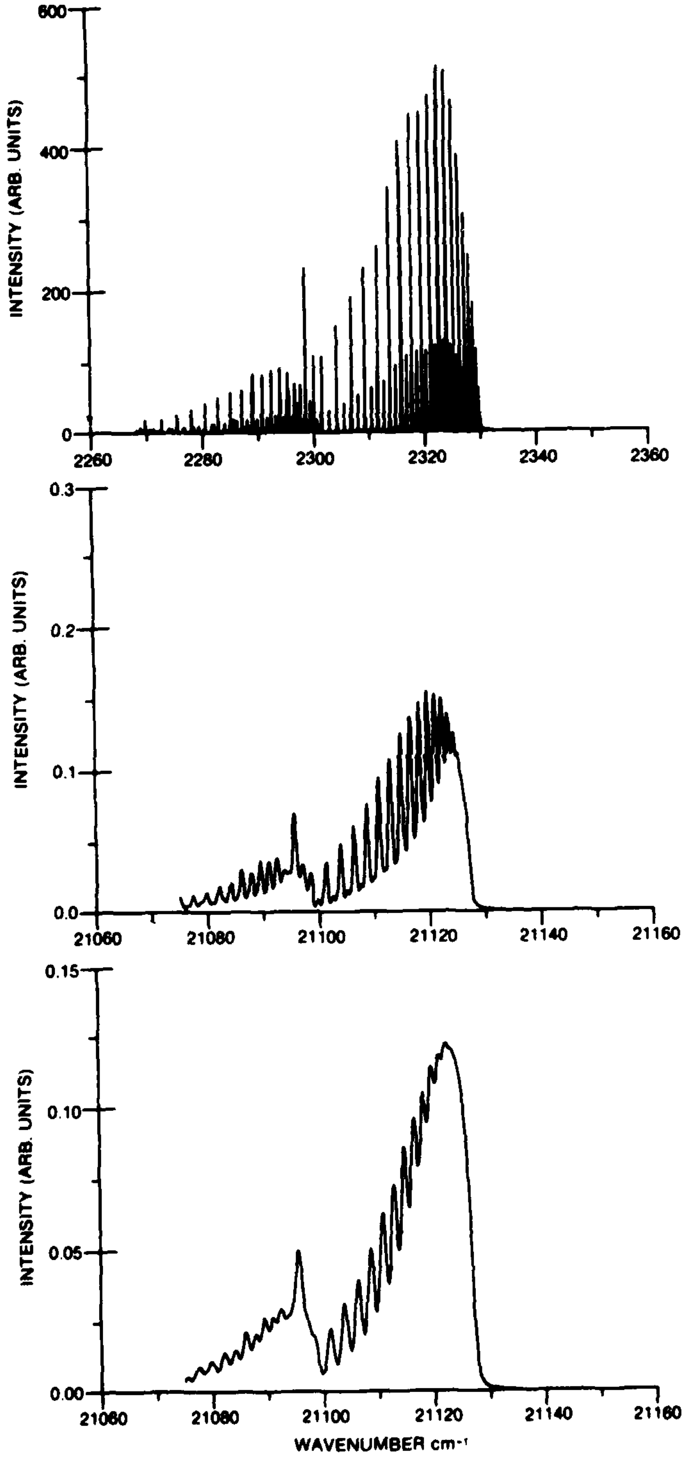

Fig 1a

Fig 1b

Fig 1c

Fig. 1

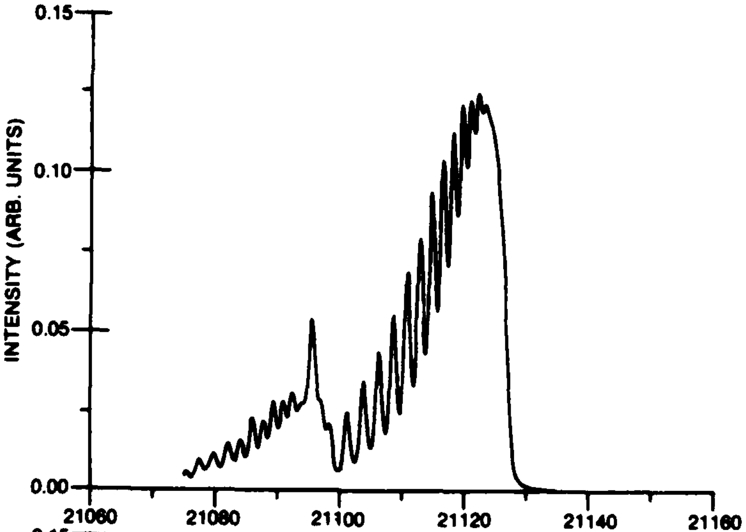

Fig 2a

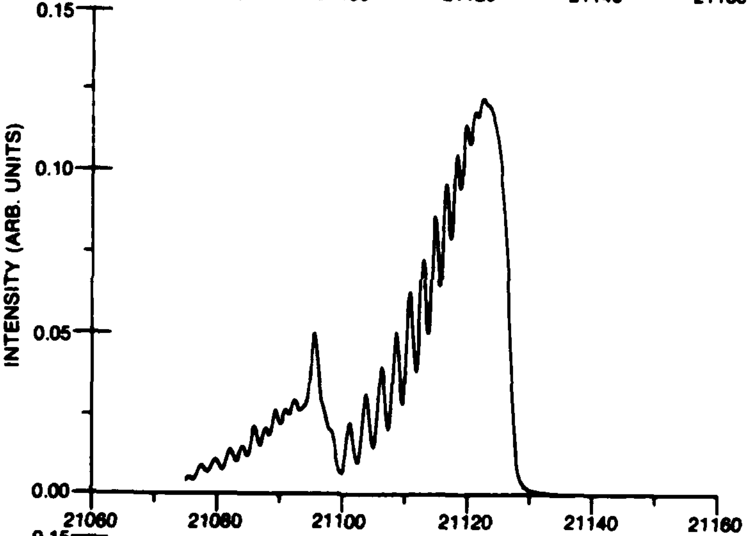

Fig 2b

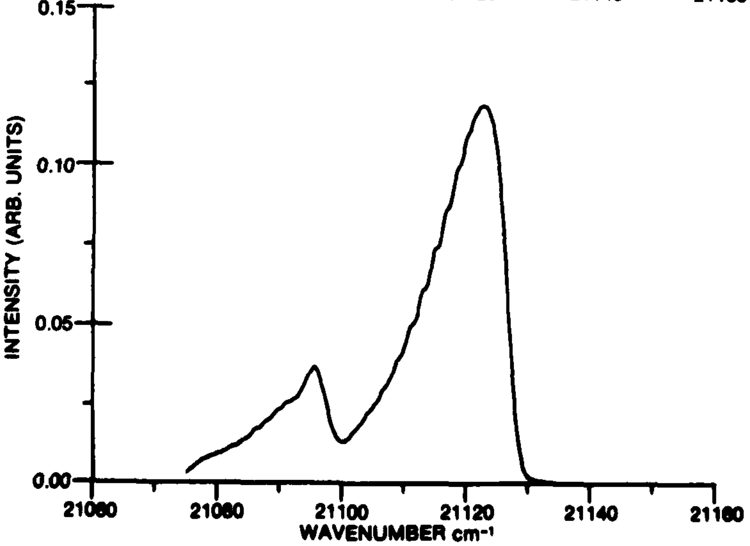

Fig 2c

Fig. 2

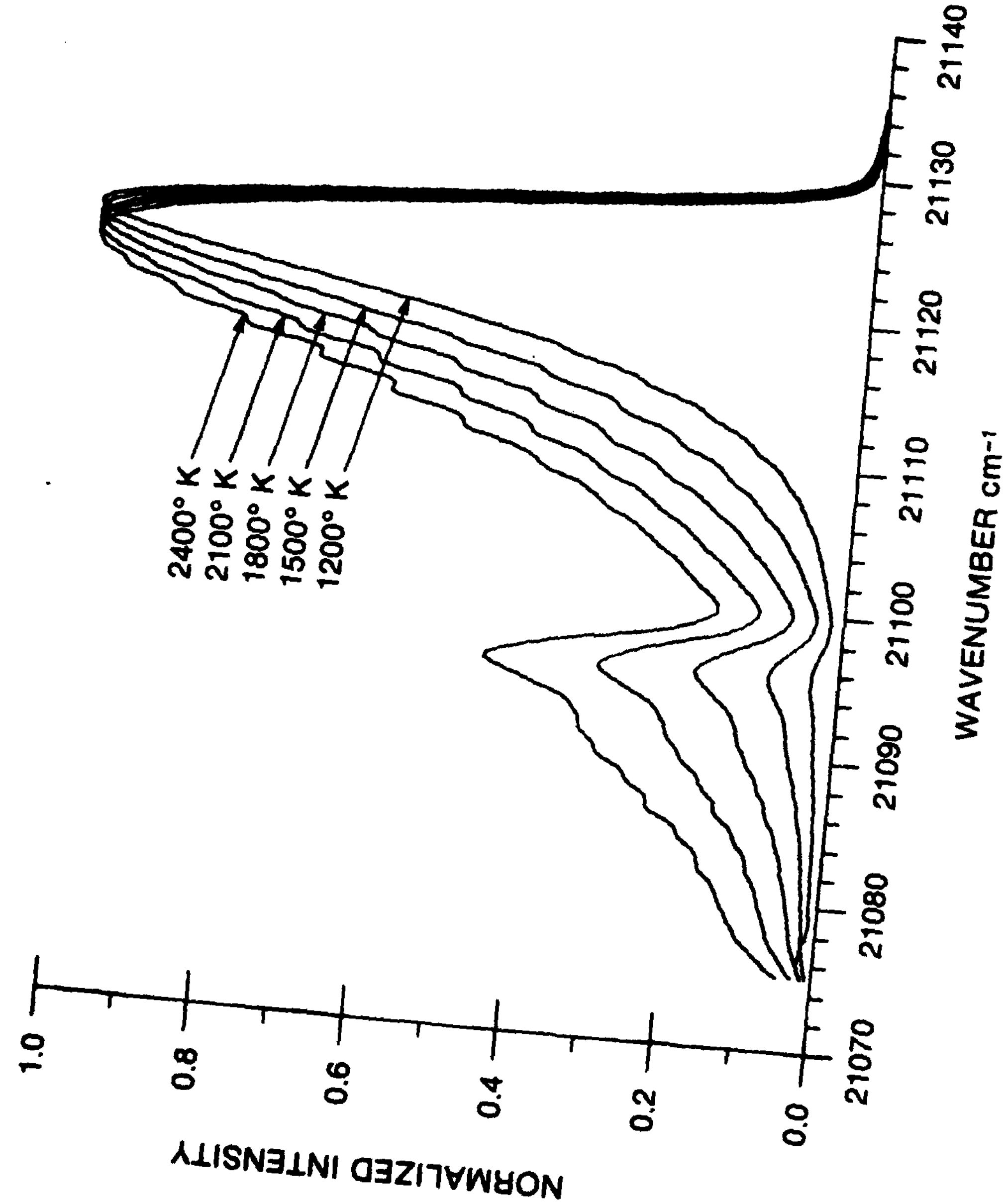
2400° K
2100° K
1800° K
1500° K
1200° K
NORMALIZED INTENSITY
1.0
0.8
0.6
0.4
0.2
0.0
WAVENUMBER cm⁻¹
21070
21080
21090
21100
21110
21120
21130
21140

Fig. 3

Unclassified

Security Classification

KEY WORDS

Coherent Anti-Stokes Raman Spectroscopy
Theory Non-Linear Polarization
Combustion Diagnostic
Nitrogen
Raman Spectroscopy

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Technical Note

5. AUTHOR(S) (Last name, first name, middle initial)

T. Parameswaran and D.R. Snelling

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13. ABSTRACT

A computer code for generating and plotting theoretical CARS (Coherent Anti-Stokes Raman Spectroscopy) spectra is described. This code, which was obtained from Dr. A.C. Eckbreth of the United Technologies Research Centre, was modified for use on a Sigma-9 computer. The theory and computational procedure involved in generating CARS spectra is discussed and the input parameters and variables used in the code are described.

Theoretical nitrogen spectra, which are presented for a range of experimental conditions are discussed.

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