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MOLECULAR BEAM CARS SPECTROSCOPY WITH
APPLICATION TO PLANETARY ATMOSPHERIC
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ULTRA HIGH RESOLUTION MOLECULAR BEAM CARS SPECTROSCOPY
WITH APPLICATION TO PLANETARY ATMOSPHERIC MOLECULES

Final Technical Report

covering the period

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Principal Investigator

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ULTRA HIGH RESOLUTION MOLECULAR BEAM CARS SPECTROSCOPY
WITH APPLICATIONS TO PLANETARY ATMOSPHERIC MOLECULES

Robert L. Byer

ABSTRACT

We have successfully demonstrated high resolution pulsed and cw CARS spectroscopy measurements in pulsed and steady state supersonic expansions. We have characterized pulsed molecular beam sources, have observed saturation of a Raman transition and have, for the first time, observed the Raman spectrum of a complex molecular cluster. We have observed cw CARS spectrum in a molecular expansion and observed the effects of transit time broadening.

Our work has established supersonic expansions as a viable technique for high resolution Raman spectroscopy of cold molecules with resolutions of 100 MHz.

ULTRA HIGH RESOLUTION MOLECULAR BEAM CARS SPECTROSCOPY WITH APPLICATIONS TO PLANETARY ATMOSPHERIC MOLECULES

Robert L. Byer

I. INTRODUCTION

This program was initiated with the goal of demonstrating high resolution spectroscopy of molecular gases under conditions encountered in planetary atmospheres.

We proposed to investigate supersonic expansions as a means of obtaining molecules of sufficient density for Raman spectroscopy but at very cold rotational temperatures.¹ Our program has succeeded to clearly show that high resolution (~ 100 MHz) Raman spectroscopy is possible on both a pulsed and cw basis of supersonic expansion cooled molecules and molecular clusters.

II. ACCOMPLISHMENTS

The key accomplishments of this research effort have recently appeared in print or are soon to be published. In this section these accomplishments are summarized. For a more complete review the publications have been included as Appendices to this report.

In 1980 we succeeded in obtaining the first CARS spectrum in a pulsed molecular beam source. The results were published in February 1981 (see Appendices 1 & 2). The key points were the development of the pulsed supersonic valve and the characterization of the expansion parameters. Also of importance was the observation that the Raman signal-to-noise was excellent

in the expansion even to equivalent rotational temperatures of a few degrees Kelvin.

The intense beams used in the CARS interaction led to the first observation of saturation in a Raman spectrum (see Appendix 3). This observation showed that a fundamental limit did exist on pumping intensities. More importantly, it opened the door for the next level of resolution in Raman spectroscopy via saturation techniques.

In mid-1981 a cw CARS experiment was attempted on a steady state CH_4 expansion. The experiment was successful and led to the first observation of cw CARS in a supersonic expansion. Preliminary results were reported at the Laser Spectroscopy Conference held in Jasper, Canada in July of 1981, (see Appendix 4).

Also reported in the conference paper was the first observation of Raman spectrum of C_2H_4 :argon clusters. This important result was published in a recent paper (see Appendix 5).

Studies of cw CARS in a supersonic expansion have continued. A soon to be published paper reports on the first observation of transit time broadening in CARS. Work is continuing on line fitting of the resolved Q-branch spectra of CH_4 , (see Appendix 6).

III. WORK TO BE COMPLETED

We have made considerable progress in lineshape theory for CARS including transit time broadening. We plan to extend our work in supersonic expansion spectroscopy using both pulsed and cw sources. Our goal is to achieve sub-Doppler resolution by saturation Raman spectroscopy. We have recently

demonstrated a less than 1 MHz linewidth Nd:YAG oscillator that is a key component of sub-Doppler CARS spectroscopy.

If research support is forthcoming we should be able to demonstrate saturation CARS spectroscopy in a molecular beam using the narrow bandwidth source within two years.

We are also preparing for publication an analysis of the JET expansion for applications to spectroscopy. This will be part of Eric Gustafson's Ph.D. thesis along with papers describing D_2 pressure broadening measurements and D_2 measurements in a 60 μ m diameter glass microsphere.

IV. REFERENCES

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2. M.D. Duncan, P. Oesterlin and R.L. Byer, "Pulsed Supersonic Molecular Beam Coherent Anti-Stokes Raman Spectroscopy of C_2H_2 ".
3. M.D. Duncan, P. Oesterlin, F. Konig and R.L. Byer, "Observation of Saturation Broadening of the Coherent Anti-Stokes Raman Spectrum (CARS) of Acetylene in a Pulsed Molecular Beam".
4. R.L. Byer, M.D. Duncan, E. Gustafson, P. Oesterlin and F. Konig, "Pulsed and cw Molecular Beam CARS Spectroscopy".
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6. E.K. Gustafson, J.C. McDaniel and R.L. Byer, "High Resolution cw CARS Spectroscopy in a Supersonic Jet".

A 100 μ sec, reliable, 10 Hz pulsed supersonic molecular beam source

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We describe a 10 Hz repetition rate, 100 μ sec duration, reliable pulsed supersonic molecular beam source. Mechanical and electrical design of the pulsed valve are given in detail. Characteristics of the supersonic expansion obtained using coherent anti-Stokes Raman spectroscopy (CARS) in acetylene are presented. They include pulse shape, gas rotational and translational cooling as a function of distance from the nozzle, clustering effects, and shock heating at the leading edge of the pulse.

I. INTRODUCTION

The unique properties of a supersonic molecular beam make it an ideal system for studying molecular properties. For spectroscopy, the substantial collisional cooling which occurs during free expansion in a supersonic molecular beam source prepares molecules in their lowest energy states and results in a greatly simplified spectrum.¹⁻⁴ The very low translational temperatures achieved encourage formation of van der Waal complexes which can be studied using a variety of techniques.^{4,5} After expansion, the cold, collision-free molecular beam can be skimmed and used as a source for scattering,⁶ photoionization,⁷ or selective excitation studies.

Until recently, however, the use of supersonic molecular beams has been limited by the cost and complexity of the required vacuum systems. In addition, the maximum achievable density of a continuous molecular beam has been kept relatively low since it is also limited by the vacuum system pumping capability. In skimmed systems a differential pumping arrangement must be used to ensure a collision-free environment for the propagating molecular beam.

The use of a pulsed molecular beam source can overcome the above limitations to a large extent. A 100 μ sec duration pulsed source operating at ten pulses per second has a duty factor of 10^{-3} compared to an equivalent density continuous source. This allows the instantaneous intensity of the pulsed source to be 100 times that of a cw source, but with only $\frac{1}{100}$ the pumping requirements. In addition, since the pressure before each pulse is low due to continuous pumping, the need for differential pumping schemes is eliminated. Each pulse expands freely into an already evacuated volume. As long as steady state expansion conditions are reached in a time short compared to the pulse length the major portion of the flow is identical to a continuous expansion.

In this paper we describe in detail a reliable, 10 Hz repetition rate pulsed molecular beam source. Both the mechanical and electrical design is discussed. In addition, detailed properties of the supersonic expansion are presented. The measurements show that steady state

conditions are reached quickly in the pulsed molecular beam.

II. THE PULSED NOZZLE

A. Introduction

Early attempts at building a pulsed molecular beam source resulted in relatively slow (> 1 msec) solenoid actuated devices.⁸ Recent designs, which achieved much shorter pulses, have been based on a pulsed valve developed by Gentry and Gieze.⁹ Pulse lengths as short as 10 μ sec have now been reached. A simple schematic of a Gentry and Gieze type pulsed valve is shown in Fig. 1. The device consists of a hairpin loop of highly conductive metal. The loop is clamped on both ends and an insulator is placed between the top and bottom pieces of the open end. A hole is drilled in the bottom plate and then sealed by an "O" ring against the upper plate. A high peak current is pulsed through the hair pin loop to activate the pulsed valve, as shown in Fig. 1(b). The current sets up opposing magnetic fields between top and bottom pieces of the hairpin and causes a displacement of the top plate. The displacement breaks the "O" ring seal and allows gas to escape from the high pressure region of the valve into a low pressure region. For short electrical current pulses, the pulse time is determined by the mechanical response of the upper plate.

Despite the simplicity and elegance of this approach, there are many problems with the original Gentry and Gieze design. Physical dimensions of the device are small to keep the inertial mass of the top plate to a minimum, but this leads to resistive heating of the plate and, therefore, a low repetition rate. Current

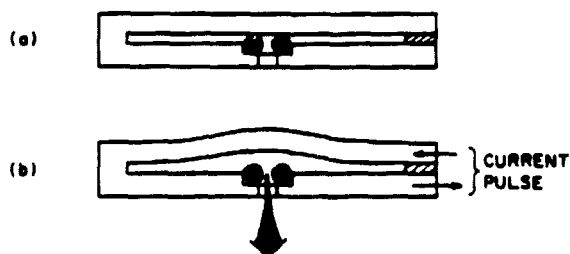


FIG. 1. Simplified diagram of a Gentry and Gieze type pulsed valve (a) closed and (b) open.

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pulses are delivered by spark-gap switched high voltages which can lead to arcing and unreliable operation. It was with these problems in mind that we decided to design an improved version of the Gentry and Gleze pulsed valve. The design goals were to produce a reliable pulsed molecular beam source which could be used in conjunction with 10 Hz repetition rate pulsed lasers. Pulse length was not critical in our applications, but pulse lengths of approximately 100 μ sec were desirable to minimize vacuum system pumping requirements. We also wanted a design that would allow the interchange of nozzles and be readily accessed for repair. Finally, we wanted to provide for gas stream flow through the valve for sampling and the possibility of heating or cooling the valve. Our original design called for operation at up to 40 atm of input pressure.

The valve described below evolved after a series of design changes in both the mechanical and electrical system. It is useful to summarize the early versions along with the reasons for later changes.

The basic mechanical design of the valve has remained as shown in Fig. 1. However, earlier versions of the valve utilized mechanically stiffer copper coated spring-steel beams and spring-steel or phosphor-bronze spring bars, machined into an "I"-beam shape for more rapid mechanical response. It was soon found that the pulse energy required to open the valve was not compatible with 10 Hz operation due to the finite conduction and limited convection cooling of the beam. This led to a mechanical design that utilized a simple bar of hardened aluminum which was more readily cooled but which also operated at longer pulse lengths.

The early electrical system used a thyatron to provide the rapid switching of the high peak current pulses. Although the thyatron was operated within its peak current and peak voltage rating, it was found not to be within its peak charge rating. The thyatron thus exhibited a short operating life of only 100 h before failing. Failure was likely due to sputtering of the control grid and loss of hydrogen gas in the tube.

A careful consideration of the peak current and voltage required for valve operation showed that a Silicon Controlled Rectifier (SCR) could be purchased that would handle the peak and average current pulses needed for valve operation. The SCR drive circuit is described below.

B. Mechanical design

Figure 2 shows an exploded view of the pulsed valve. The main components are, from top to bottom on the diagram, spring bar (A), Mylar insulator (B), copper base bar (C), Mylar insulator (D), "O" ring (E), stainless steel base plate (F), removable nozzle (G), and nozzle retaining ring (H). The end clamps (I), which hold both ends of the bar assembly tightly down, are shown above the spring bar. Two feed throughs (J) on one side of the base plate provide for current input and output. One feed through is simply a copper rod brazed in a hole in the base plate. Electrical contacts are made between top and bottom bars by a copper shim located on

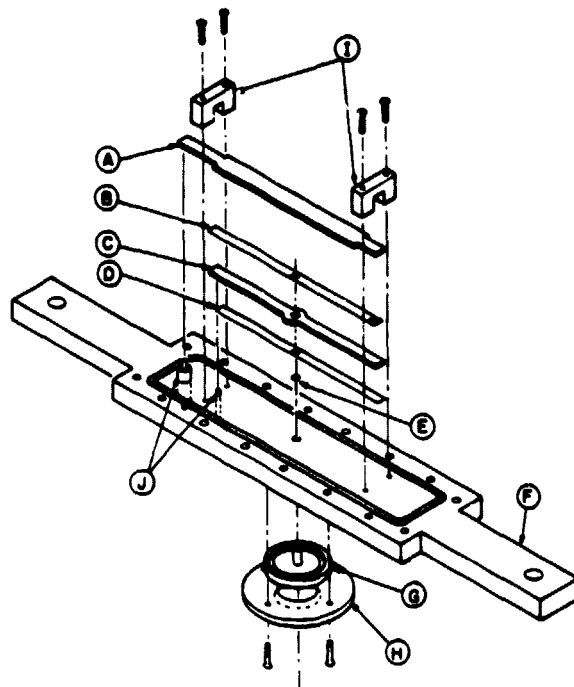


FIG. 2. Exploded view of pulsed valve.

the opposite side from the feed throughs. The thickness of the Mylar insulator between top and bottom bars is 0.05 mm (0.002 in.) and the thickness of the Mylar insulation between base bar and base plate is 0.175 mm (0.007 in.). The end clamps are insulated by Mylar glued to their arches. The nozzle assembly inserts and makes an "O" ring seal with the base plate. The neck of the nozzle comes flush with the inside surface of the baseplate and seals against a number 001 "O" ring. This small "O" ring fits within a hole made in the base bar and both insulating strips and seals against the under side of the spring bar.

The "O" ring has an i.d. of 0.71 mm (0.029 in.) and a cross section of 0.98 mm (0.040 in.). The spring is 3.8 cm long, 3 mm wide, and 0.5 mm thick, with a mechanically active length of approximately 3 cm. The copper base bar has equivalent dimensions except for the bulge around the "O" ring hole. The 0.635 cm (0.25 in.) thick stainless steel base plate is 19 cm long (7.5 in.) and has mounting holes drilled on either end. The main body of the base plate supports a rectangular "O" ring which forms a vacuum seal with a large water cooled solid copper body. The copper body has gas inlet and outlet lines and supports enough connecting bolts to allow operation at 40 atm plenum pressure. The total enclosed space in the valve, once connected with the copper body, is approximately 10 cm³.

Figure 3 shows two photographs of the pulsed valve assembly. Figure 3(a) shows the base plate with the assembled mechanical pieces and the copper body with water and gas lines. Figure 3(b) shows the valve completely assembled and shows the nozzle assembly. A conical nozzle is shown in this photograph, but other nozzle shapes are also commonly used. At present the

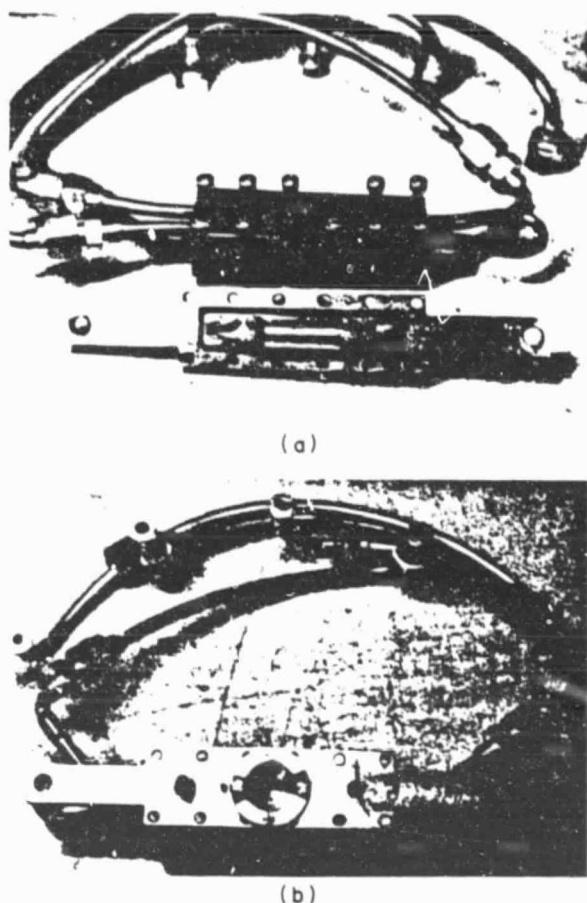


FIG. 3. Photographs of (a) assembled internal components of the pulsed valve and (b) assembled valve showing nozzle.

valve operates with a flat nozzle with a straight cylindrical channel 6 mm long and 0.5 mm in diameter.

The actual spring bar material used is 6061T6 aluminum. This material was chosen because of its low density, fairly high stiffness, and good electrical and heat conductivities. When struck by an impulse force caused by opposing magnetic fields, the spring bar responds with its natural frequency and executes sinusoidal motion. Only one-half of a natural vibration can occur due to contact with the "O" ring. Using a well known formula for the mechanical response of a beam with both ends clamped, we can calculate the natural beam oscillation frequency. It is given by¹⁰

$$f = 4.73^2 / 2L^2 (EI / \rho A) \quad (1)$$

where f is frequency, L the length of the beam, ρ the density, A the cross-sectional area, E Young's modulus, I the two dimensional moment of inertia, and λ a constant which is 4.73 for the lowest natural frequency of the beam.

Using the dimensions given above for our spring bar, and using mechanical constants for half-hardened aluminum, we find that Eq. (1) gives a frequency of 452 Hz, or a half-cycle response time of 110 μ sec. In practice the spring bar is bent downward slightly so that it makes

a good seal with the "O" ring. This stress biases the response of the bar so that it requires a large impulse to open. It also slightly reduces the response time.

C. Electrical design

The schematic for the pulsed valve electrical circuitry is shown in Fig. 4. A pulse charging power supply is used to charge a 35 μ F capacitor to voltages up to 1000 V. A large hockey-puck silicon controlled rectifier (International Rectifier #600 PBQ 180) is used to discharge the capacitor and allow a high peak current pulse to flow through the conductors of the pulsed valve. A 2 μ H inductor is added to the circuit to limit the rate of current change di/dt to a value consistent with the SCR specifications (800 A/ μ sec). A diode is included in the front end of the circuit to prevent the capacitor from seeing damaging reverse voltage swings. A snubber circuit is used to prevent high voltage spikes and a large trigger signal is used to assure uniform SCR turn on.

A typical electrical pulse produced by the circuit is 30 μ sec long and reaches a peak current of 2500 A for a 600 V charging voltage. The energy per pulse is 6.3 J, giving a power dissipation throughout the circuit of 63 W at a 10 Hz repetition rate. Electrical connection is made to the pulsed valve by a few feet of heavy gauge wire which is either in a twisted pair or coaxial arrangement. The SCR switch has proven to be very reliable over six months of operation.

The resistive heating produced in the active parts of the valve during a current pulse can be calculated. It is approximately 2.5 W for the aluminum spring bar and 1.0 W for the base bar at 10 Hz repetition rate. Thermal conductivity is good in both of these components so that there is no problem with local heating. Overall heating of the valve is not a problem due to the water cooled copper body. Without water flow the valve slowly heats up until the thin Mylar insulation between spring and base bars melts. This results in an electrical short. Reliability of the valve is good as long as it is cooled. We estimate that the lifetime for the mechanical parts of the valve is 5×10^7 shots. To date mechanical wear and arcing have not been observed. The only failure of the valve occurred due to inadvertent lack of water cooling. There have been no problems with the solid state driving electronics where operation lifetimes of the SCR and capacitor are expected to be in excess of 10^6 shots.

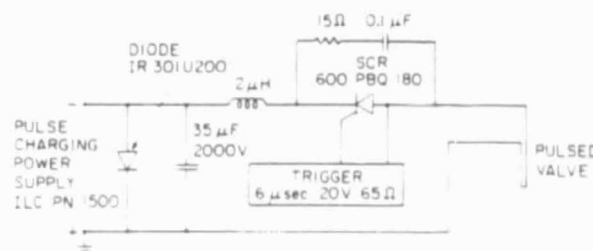


FIG. 4. Pulsed valve electronics

D. Design considerations

The mechanical response of the pulsed valve is not instantaneous. At a driving voltage of 600 V a delay of 70 μ sec between electrical pulse and gas pulse is seen. This delay is caused primarily by the inertia of the spring bar and indicates that it is not the peak value of the current pulse that drives the bar but rather the total impulse. This fact can be used to advantage in systems with mechanical response times greater than 50 μ sec by allowing a longer electrical pulse at a lower voltage to achieve the same mechanical displacement as shorter, higher voltage pulses. The only criterion to be met is that the electrical pulse be shorter than the mechanical response time.

The design of the present pulsed valve indicates that a valve with shorter open times should be possible to construct. The natural frequency of the spring bar is given by Eq. (1) and is proportional to $(I/A)^{1/2}$, where A is the cross-sectional area of the beam and I is the two dimensional moment of inertia. For a rectangular $I = bh^3/3$, where b is the width and h the height of the bar. This gives the simple relation that frequency is proportional to the height of the spring bar and that doubling the thickness of our present spring bar would give a 50 μ sec response time. The energy needed to provide deflections of the thicker bar equal to deflections of the thin bar now in use would be increased four times, giving twice the present voltage and approximately twice the present heating. This does not present a problem since all parameters for the present valve are two or three times below maximum ratings for electrical components. The water cooling is capable of handling the increased heat load easily.

III. GAS PULSE AND SUPERSONIC EXPANSION PROPERTIES

The pulsed valve discussed in this paper was developed specifically for use in a laser spectroscopy experiment using the CARS technique.¹¹ The ν_2 Q branch of acetylene (C_2H_2) was initially studied. The spectrally resolved Q branch structure of acetylene provided an excellent indication of local rotational temperature. The complete experimental apparatus is described elsewhere¹ and only the parts relating to molecular beam parameters are discussed here.

The pulsed valve is mounted on an x - y translation stage in the center of a 1 m diam, 0.5 m high vacuum chamber. Stationary lenses focus and recollimate the interacting laser beams. The laser beams propagate transverse to gas flows. The face of the valve can be brought to within 1 mm of the focused laser beams or can be moved up to 10 cm away. The vacuum system is pumped by a single 6 in. diffusion pump with liquid nitrogen cold trap. The approximate pumping speed is 650 l/sec. A quadrupole mass spectrometer used for molecular species diagnostics is also in the molecular beam line.

The pulsed valve is typically operated with 1–5 atm of gas in the valve body. No leakage is observed when the valve is not pulsed, and an average vacuum of 3

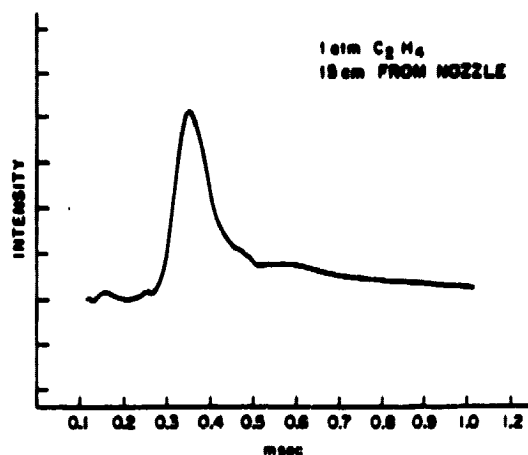


FIG. 5. "Nude" ionization gauge signal of gas pulse from pulsed valve. Gauge was 15 cm from the valve nozzle and source pressure was 1 atm of ethylene (C_2H_4).

$\times 10^{-4}$ Torr is maintained during operation. The pressure is low enough and distance long enough so that the molecular beam properties observed are completely unaffected by background gas or scattered molecules. A gas pulse from the valve is shown in Fig. 5. This measurement was made by monitoring the output of a "nude" ionization gauge 15 cm from the valve. The measured pulse length is very close to the expected 110 μ sec long pulse predicted from Eq. (1). This pulse length is typical of most medium sized molecules at 1–10 atm plenum pressures.

To be equivalent to a continuous flow, pulses from the pulsed valve must reach the "choked" flow regime.¹² This condition occurs when the valve has opened sufficiently far to allow pressure limited gas flow through the nozzle and is indicated by flat-topped pulses. Figure 6 shows observation of such flat-topped pulses. The method of obtaining pulse shapes was to delay the pulsed valve opening relative to the pulsed lasers and observed the actual CARS signal as a function of the delay. Modulation of the flat top is seen and may be indicative of density fluctuations. The flat top of both (a) and (b) indicates that the valve has opened fully and that gas flow is limited by pressure alone. Part (b) shows that as voltage to the valve is increased the choked flow region of the pulse lengthens, as it should, since the spring bar is driven further from the "O"-ring seal. Normally the pulsed valve is operated at 1.5 times the threshold voltage to insure steady state flow and to increase pulse-to-pulse stability.

Expansion from a nozzle source into high vacuum results in adiabatic cooling of the molecular flow. This cooling is a real reduction in Maxwellian velocity distribution relative to the center of mass flow velocity. Well known continuum expansions equations describe this process very well. The temperature and density are given by¹¹

$$T = T_0 \left[1 + \frac{1}{2} (\gamma - 1) M^2 \right], \quad (2)$$

$$\rho = \rho_0 \left[1 + \frac{1}{2} (\gamma - 1) M^2 \right]^{1/(1-\gamma)}, \quad (3)$$

where

$$M = A \left(\frac{X - X_0}{D} \right)^{-1} - \frac{1}{2} \left(\frac{\gamma + 1}{\gamma - 1} \right) / A \left(\frac{X - X_0}{D} \right)^{-1} \quad (4)$$

and T_0 is the initial temperature, ρ_0 the initial density, γ the molecular ratio of specific heats, D the nozzle diameter, X the distance from the nozzle, A a constant which depends on γ , and X_0 an experimentally derived constant. Rotational degrees of freedom thermally equilibrate very quickly with the translational degrees of freedom in the expansion and become a very good probe of temperature of the expansion.

Figure 7 shows a sequence of spectra of the ν_2 Q branch of acetylene taken by using the CARS technique. Figure 7(a) is a scan taken in room temperature static gas showing clearly the temperature of the gas by its rotational Boltzmann distribution. Acetylene has a nuclear spin degeneracy factor of 3:1 for odd:even rotational states and this ratio is enhanced to 9:1 by the CARS process. Figure 7(b) is a scan taken in the molecular beam 2.5 mm, or at an X/D of 5, away from the nozzle. Cooling is indicated by the shift in peak rotational population and the spectrum is fitted nicely using an 80°K temperature. Farther along in the expansion, at $X/D = 20$, temperature has dropped to 30°K, as is indicated in Fig. 7(c).

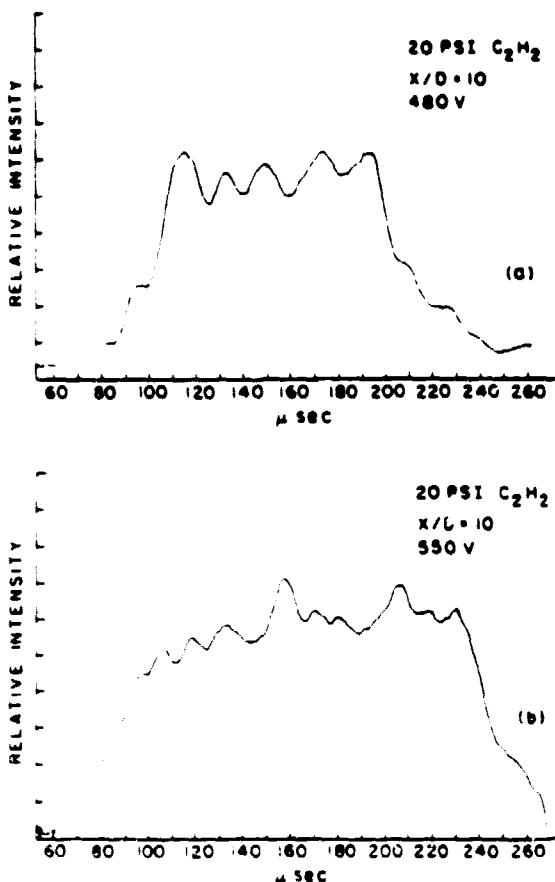


FIG. 6. Gas pulses from the pulsed valve operated at (a) 480 V and (b) at 550 V. The flat top on the pulses indicated choked flow.

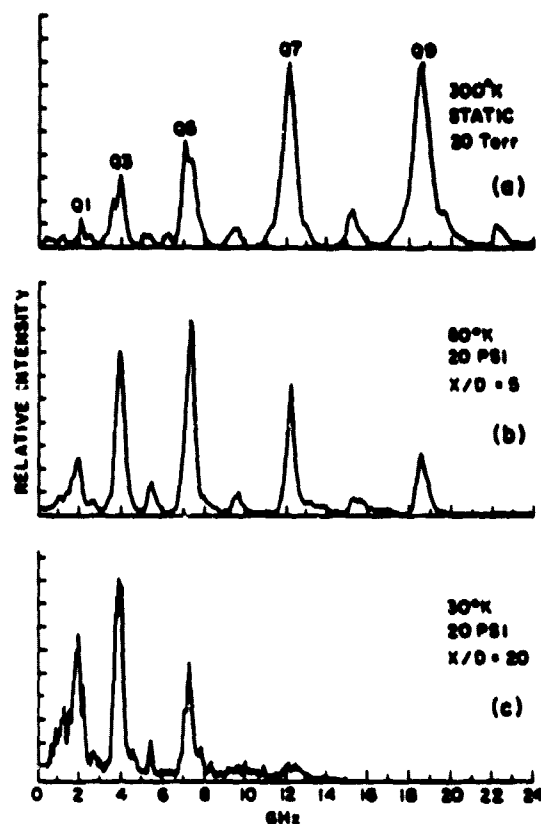


FIG. 7. Spectra of the ν_2 Q branch of acetylene taken with the CARS technique in (a) static gas, (b) in the molecular beam at $X/D = 5$, and (c) in the molecular beam at $X/D = 20$.

A systematic study of expansion rotational temperature for acetylene vs distance from the nozzle was undertaken and the results are shown in Fig. 8. Also shown are theoretical plots of temperature vs X/D for two different γ 's. The $\gamma = 7/5$ line corresponds to the cooling which is predicted for acetylene using Eq. (2) and the $\gamma = 5/3$ line is the predicted cooling for a noble gas. Data for acetylene at 20 and 40 psi plenum pres-

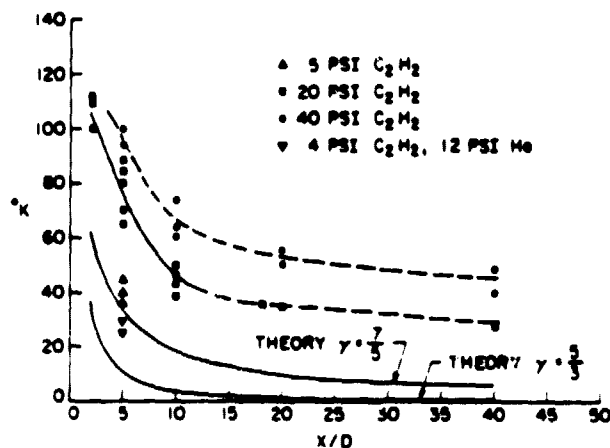


FIG. 8. Plot of rotational temperature in the supersonic expansion versus X/D . Theoretical curves for gases with $\gamma = 7/5$ and $\gamma = 5/3$ are shown.

sure indicate that the actual cooling in the supersonic expansion is not as great as predicted by theory. This is explained by attributing the temperature discrepancy to heating effects due to clustering. Clustering can occur in a cooling expansion whenever the local temperature has dropped below the boiling point for the expanding gas and local density is high enough to support three-body collisions. Dimers, trimers, and larger clusters form in the low temperature, high density gas and their heat of formation is released into the expansion. The subsequent cooling produced in the expansion reaches a temperature higher than predicted by theory. The boiling point of acetylene is 190°K and is reached very quickly in our expansion, indicating that clustering is the cause of the high expansion temperatures. This is verified by the magnitude of the effect as a function of temperature. The heating should be less severe as the plenum pressure is lowered since this reduces the expansion density. This is indeed the case as indicated by the data in Fig. 8. Expansion temperatures decrease as the plenum pressure is reduced from 40 to 20 psi and measurements at 5 psi indicate that the cooling is almost as great as predicted by theory. Cluster formation is also verified by mass spectrometer data which indicates a 4 and 8% density of dimers in the expansion at 20 and 40 psi plenum pressures, respectively.

Expansion temperatures can be controlled to some extent by the addition of a noble gas, such as helium, to the plenum gas. The noble gas has a γ of 5/3 and cools much more effectively in the expansion, as is shown by the cooling curve for $\gamma = 5/3$ in Fig. 8. For large ratios of helium to the gas of interest, expansion temperatures of less than 1°K can be achieved.¹³ The effect is shown in Fig. 8 for a moderate ratio of 3:1 helium to acetylene where temperatures below those predicted for acetylene alone are achieved.

Density in the supersonic molecular beam cannot be measured accurately using the CARS technique. Values of density, based on signal strength or signal-to-noise ratios, are only approximate. A somewhat more accurate measurement of density can be made using a calibrated ionization gauge. All measurements made in that way agree well with the density predicted by Eq. (3).

An interesting feature of pulsed molecular beam is the possibility of shock heating during the leading edge of a gas pulse. Shock heating is caused by the interaction of the pulse with low density background gas. This effect was predicted¹⁴ by analogy with classical gas dynamic shock tubes. In a shock tube a high pressure gas is suddenly allowed to expand into a low pressure region. The expanding gas shocks against the "stationary" gas in the low pressure region and causes a large heating to occur in the leading edge of the expansion. In the case of the pulsed valve the expanding supersonic molecular beam shocks against the low pressure background gas and heats the beginning of the pulse.

Shock heating is indeed observed in our pulsed molecular beam. Pulsed valve opening times are delayed relative to the laser interaction time and rotational spectra of the low density leading edge of the gas pulse

are obtained. Temperature measurements from these spectra indicate that gas temperatures are four times higher in the first 15 μ sec of the gas pulse than predicted by Eq. (2). The density of gas is so low that clustering is not significant, so the heating must be attributed to shock effects.

IV. CONCLUSION

In this paper we have presented in detail the design and characteristics of a pulsed, supersonic molecular beam source. Improvements in this source over previously built pulsed molecular beam sources includes high repetition rate, simple mechanical design, reliable operation and low voltage, solid state driving electronics. Characteristics of the source have been obtained in large part by using rotational temperatures of the expanding molecular beam derived from the rotational spectra of acetylene. These characteristics have been shown to follow theoretical predictions for low source pressures but are seen to be modified at high source pressures by clustering and shock heating.

The design and characteristics of this reliable, 10 Hz repetition rate pulsed molecular beam source should encourage the use of pulsed, supersonic molecular beams in an increasing number of applications.

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Pulsed supersonic molecular-beam coherent anti-Stokes Raman spectroscopy of C_2H_2

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We have obtained a high-resolution coherent anti-Stokes Raman spectrum of C_2H_2 in a pulsed molecular beam and have used the resolved Q -branch spectrum to study the properties of the expansion. Cluster formation limited the minimum observed rotational temperature in the pure-acetylene expansion to 30 K.

The possibility of performing high-resolution coherent anti-Stokes Raman spectroscopy (CARS) in a molecular beam was theoretically investigated over one year ago by Duncan and Byer.¹ In this Letter we report the first known high-resolution CARS in a pulsed supersonic molecular beam.

The advantages of Raman spectroscopy in a molecular beam include increased signal resulting from spectral simplification from rotational cooling on expansion, sub-Doppler linewidths, and the possibility of studying complex molecules. Initial estimates of the required laser power and expected signal-to-noise ratio were promising but not encouraging.¹

Recent advances in pulsed nozzle sources² and in high-power single-mode laser sources^{3,4} have made CARS and Raman-gain spectroscopy in molecular beams possible. Low-resolution CARS of a continuous nitrogen supersonic flow has been demonstrated,⁵ and recently cw CARS measurements of CH_4 have been obtained in a continuous supersonic flow.⁶ Almost coincidentally with this work, Valentini *et al.*⁷ have obtained high-resolution inverse Raman gain spectra of CH_4 in a continuous supersonic jet.

The high molecular density in a pulsed supersonic flow and the reduced vacuum-system pumping requirements are advantageous for molecular-beam CARS studies. In addition, the unique properties of the pulsed supersonic jet make it an interesting topic for further study. Acetylene was chosen for this study because its resolved Q branch⁸ is an ideal probe of the supersonic jet parameters. In addition to linewidth-narrowing effects, we report measurements of rotational temperature cooling versus plenum pressure and distance from the nozzle and rotational heating from cluster formation.

The experimental apparatus shown in Fig. 1 consists of three principal subsystems: a pulsed molecular-beam source (pulsed valve), a single axial-mode unstable Nd:YAG oscillator, and a Nd:YAG-pumped dye amplifier chain. The Q -switched unstable-resonator Nd:YAG oscillator is operated in a stable single axial mode by a recently demonstrated injection-locking technique.^{4,9} 1 μ J of energy from a non- Q -switched single-axial-mode TEM₀₀-mode Nd:YAG oscillator is injected into the unstable-resonator oscillator, leading

to single axial-mode operation at 200-mJ output energy with a Fourier-transform-limited linewidth of less than 100 MHz. The output of the unstable resonator oscillator is split, amplified, and frequency doubled in KD*P. One green beam is used for the pump in the CARS interaction. The second beam is used to pump a three-stage dye-amplifier chain, which amplifies a 100-mW cw dye laser up to 1-MW, 4-nsec, Fourier-transform-limited pulses with a bandwidth of 140 MHz.³ The dye-laser source is tuned to the Stokes frequency and combined collinearly with the pump beam. Both are focused tightly into a region in front of the pulsed nozzle.

The pulsed nozzle is an improved version of the original Gentry and Giese design.² It operates by magnetic repulsion of a spring bar, which sits above an O-ring seal. A 30- μ sec, high-current pulse opens the valve and allows the gas to flow into a cylindrical channel 6 mm long by 0.5 mm in diameter. The 100- μ sec-long, 10-Hz repetition-rate pulses expand into a

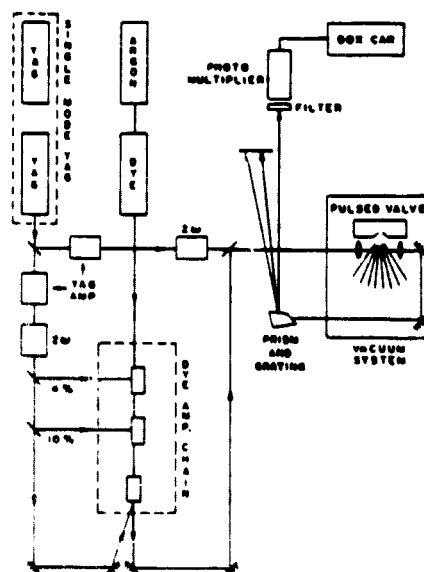


Fig. 1. Experimental arrangement for recording pulsed supersonic molecular-beam CARS spectra.

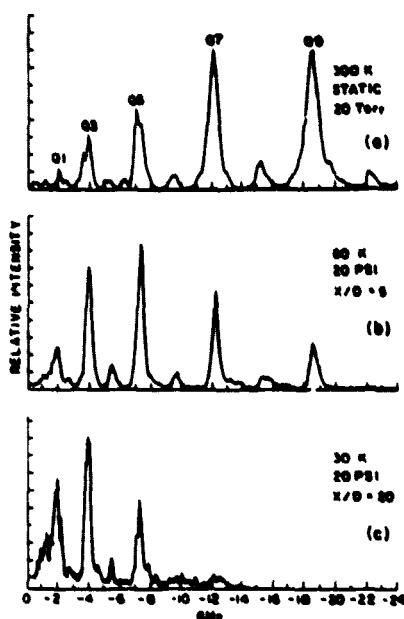


Fig. 2. CARS spectra of the ν_2 Q branch of acetylene at 1974 cm^{-1} . (a) Static gas: 20-Torr pressure, 300 K. (b) Pulsed supersonic jet: 20-psi backing pressure, 80 K; <0.5-mJ, 0.5320- μm energy. (c) Pulsed supersonic jet: 20-psi backing pressure; 30K; <0.5-mJ, 0.5320- μm energy.

3×10^{-4} -Torr vacuum, which is maintained by a small, 15.24-cm-diameter diffusion pump. The pulsed nozzle is mounted on a translation stage, which allows measurements to be made at various distances from the nozzle.

For the measurements reported here, pure acetylene at plenum pressures up to 4 atm was used. The laser beams propagated transversely to the molecular-beam axis and were focused to a 30- μm -diameter spot in front of the nozzle. The generated anti-Stokes beam was separated by prism- and grating-dispersing elements, passed through a spike filter, and directed onto a photomultiplier cathode. Background and scattered light were not a problem. The signal was processed by a boxcar integrator and fed to a minicomputer for storage, plotting, and analysis.

Figure 2(a) shows a resolved ν_2 Q-branch spectrum of acetylene taken at 20 Torr in static gas. The even-odd 1:3 nuclear-spin degeneracy factor, enhanced to 1:9 by the nonlinear CARS response, is clearly seen. This 300-K scan has a 143-MHz FWHM Doppler-width contribution to the measured linewidth of 400 MHz. The dye-laser linewidth and ± 50 -MHz frequency jitter of the Nd:YAG laser that is due to thermally induced cavity-length changes contribute to the observed linewidth. Saturation broadening and ac Stark broadening also contribute to the measured linewidth.

Figure 2(b) shows the acetylene spectrum in the pulsed molecular beam at a distance 2.5 mm or five nozzle diameters downstream from the nozzle. A significant decrease in the rotational temperature is evi-

dent, as is a reduction in the linewidth from 400 to 300 MHz. Figure 2(c) shows the spectrum at a distance 10 mm or 20 nozzle diameters from the nozzle. At this distance, the effective gas density is only 0.2 Torr, and the gas has nearly achieved its maximum cooling.

Spectra were taken at a series of distances from the nozzle so that temperature could be accurately determined and compared with the well-known continuum-expansion equation for supersonic flow¹⁰ given by

$$T = T_0/[1 + \frac{1}{2}(\gamma - 1)M^2], \quad (1)$$

where

$$M = A \left(\frac{X - X_0}{D} \right)^{\gamma-1} - \frac{1}{2} \frac{(\gamma + 1)}{(\gamma - 1)} \left[A \left(\frac{X - X_0}{D} \right)^{\gamma-1} \right]^{-1} \quad (2)$$

is the Mach number, γ is the ratio of specific heats, A is a constant determined by γ , X is the distance, D is the nozzle diameter, and X_0 is an experimentally determined constant. In the present expansion, $\gamma = 7/5$ (rotational degrees of freedom only). The nuclear-spin states remain at room temperature throughout the expansion.

Figure 3 shows a plot of the measured and theoretically predicted rotational temperatures versus distance from the nozzle. The measured temperatures at large X/D are approximately 20 K above the predicted temperature for 20-psi and 40 K above for 40-psi acetylene pressures. We attribute this temperature discrepancy to dimer and larger cluster formation with a resultant heat release.¹¹ This is verified by a low-pressure expansion at 5 psi, which, for $X/D = 5$, falls very close to the theoretical curve. We have looked for acetylene dimers with a mass spectrometer and have found approximately 4 and 8% for 20- and 40-psi pressures. From this dimer-formation percentage (a lower bound) and from the measured temperature difference, we estimate that the acetylene van der Waals dimer binding energy is approximately 390 cm^{-1} .

We have looked for and observed an increase in acetylene temperature near the leading edge of the

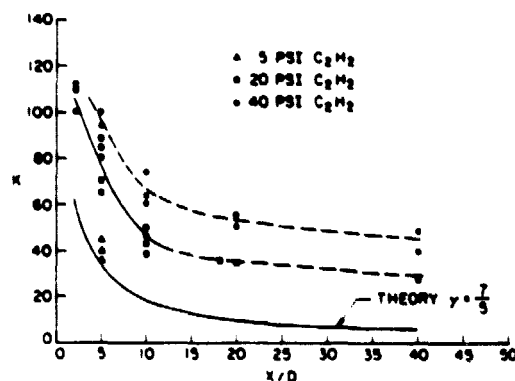


Fig. 3. Plot of temperature versus distance from a supersonic nozzle. Distance is given in units of D , the nozzle diameter. $D = 0.5$ mm, and initial temperature was 300 K.

100- μ sec pulse. This temperature increase was predicted¹² by analogy with shock-tube behavior. The measured shock temperature was 40% greater than the steady-state temperature obtained in the rest of the gas pulse.

The combination of a pulsed, supersonic molecular beam and its increased gas density, greatly reduced pumping requirements, and spectral simplification because of expansion cooling, together with coherent Raman spectroscopic techniques, provides for the first time to our knowledge the possibility of performing high-resolution Raman studies of complex molecules. The present experiment demonstrates that molecular-beam CARS has more than adequate signal-to-noise ratio and resolution to become a useful spectroscopic tool for these studies.

We want to acknowledge the assistance of Isaac Bass and Frederick Konig, the assistance of M. A. Henesian for use of his CARS line-shape theory and program, and the support provided by the National Aeronautics and Space Administration through contract NSG2372 and the National Science Foundation through contract CHE791-12673.

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APPENDIX 3

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CHEMICAL PHYSICS LETTERS

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OBSERVATION OF SATURATION BROADENING OF THE COHERENT ANTI-STOKES RAMAN SPECTRUM (CARS) OF ACETYLENE IN A PULSED MOLECULAR BEAM

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Reported is the first observation of saturation broadening in a high-resolution coherent Raman spectrum of the ν_2 Q-branch of acetylene. The measured saturation broadening of 1050 MHz is significantly greater than the calculated ac Stark broadening of less than 100 MHz.

In this letter we report the observation of saturation broadening in the high-resolution coherent Raman spectrum of acetylene. Saturation effects have been observed and studied in dipole allowed [1] and even two-photon spectroscopy [2], but not until the advent of high peak power lasers and coherent Raman spectroscopic techniques has saturation become important in Raman spectroscopy. Saturation has been discussed in relation to stimulated Raman gain spectroscopy [3] (SRGS) and coherent and anti-Stokes Raman spectroscopy [4] (CARS), but no attempt has been made to measure or calculate its effect on linewidths. Recently saturation has been proposed [5] and used [3] in a Raman analog to normal saturation spectroscopy.

In this letter we present calculations which describe the effect of saturation broadening on spectra obtained using the CARS technique and present experimental data showing saturation broadening on spectral linewidths of the ν_2 Q-branch of acetylene. Saturation occurs in a CARS interaction when there is sufficient perturbation of the molecular ground-state population due to stimulated Raman scattering (SRS).

The CARS signal strength for a low-density gas is given by [6]

$$P_{as} = (8\pi^2 c^2 \omega_{as} / \hbar \omega_p \omega_s^3)^2 (\Delta N)^2 (d\sigma/d\Omega)^2 \times I_p^2 P_s L^2 [1/(2\Delta\omega^2 + \Gamma^2)], \quad (1)$$

where ω_{as} , ω_s and ω_p are anti-Stokes, Stokes and pump frequencies, ΔN is the population difference between ground and excited molecular states, $d\sigma/d\Omega$ is the spontaneous Raman scattering cross section, I_p is the pump laser intensity, P_s is the Stokes laser power, L is the interaction length, $\Delta\omega$ is a detuning factor given by $\omega - (\omega_p - \omega_s)$ where ω is the molecular transition frequency of interest, and Γ is a convolution of all natural and laser linewidth factors. SRS occurs simultaneously with the CARS process and may significantly affect the population difference ΔN , at high laser intensities. For the case of pulsed lasers with pulse lengths less than population decay rates, the transient perturbation of ΔN caused by SRS is described by

$$d(\Delta N)/dt = -(\Delta N)(8\pi^2 c^2 / \hbar^2 \omega_p \omega_s^3)(d\sigma/d\Omega) \times I_p I_s [\Gamma/(\Delta\omega^2 + \Gamma^2)], \quad (2)$$

where I_s is the Stokes laser intensity and all other quantities have been defined previously. Saturation causes a decrease in ΔN and hence in the CARS signal on line center, as can be seen from eq. (2), but causes a smaller decrease off line center. This has the effect

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of flattening and broadening a line. Eq. (2) can be integrated to give

$$\Delta N = \Delta N_0 \exp \{-A I_p I_s [\Gamma / (\Delta \omega^2 + \Gamma^2)] t\}. \quad (3)$$

where ΔN_0 is the population difference before the laser interaction and

$$A = (8\pi^2 c^2 / \hbar^2 \omega_p \omega_s^3) d\sigma / d\Omega$$

is the interaction constant. Damping terms have been left out of eq. (2) since typical radiative decay lifetimes and low-pressure collisional lifetimes are assumed to be greater than the laser pulse widths.

Eq. (3) must be integrated over the interaction time τ to determine the population perturbation effects on the CARS signal strength. The result after squaring is

$$\frac{(\Delta N)^2}{(\Delta N_0)^2} = \frac{1 - \exp \{-2A I_p I_s [\Gamma / (\Delta \omega^2 + \Gamma^2)] \tau\}}{2A I_p I_s [\Gamma / (\Delta \omega^2 + \Gamma^2)] \tau}. \quad (4)$$

We can obtain an approximate value for the saturation linewidth by using eq. (4) as a multiplicative factor in eq. (1) to obtain the signal maximum, I_{as} , and signal half maximum $\frac{1}{2} I_{as}$ as a function of I_p , I_s and detuning $\Delta \omega$. Combining these equations we obtain

$$\frac{1 - \exp \{-2A I_p I_s \tau / \Gamma\}}{1 - \exp \{-2A I_p I_s [\Gamma / (\Delta \omega_{1/2}^2 + \Gamma^2)] \tau\}} = \frac{2\Delta \omega_{1/2}^2 + 2\Gamma^2}{2\Delta \omega_{1/2}^2 + \Gamma^2}. \quad (5)$$

where $\Delta \omega_{1/2}$ is the detuning needed to achieve $\frac{1}{2} I_{as}$. This equation must be solved iteratively to find values of $\Delta \omega_{1/2}$ as a function of I_p and I_s . The fwhm broadening due to saturation is $2\Delta \omega_{1/2}$.

Eq. (5) is useful for obtaining an approximate saturation broadened linewidth. However, to predict the effect of saturation on the CARS lineshape at arbitrary detuning or for complex spectra a more detailed theoretical treatment must be followed which couples the stimulated Raman induced population change with the CARS lineshape theory [7,8].

The experimental apparatus used to observe saturation in a CARS interaction is shown in fig. 1. The apparatus was designed to allow high-resolution Raman studies of molecules in a supersonic molecular beam and is described in more detail elsewhere [9]. The apparatus consists of three principal subsystems: a pulsed molecular beam source ("pulsed valve"), a single axial mode unstable Nd:YAG oscillator [10],

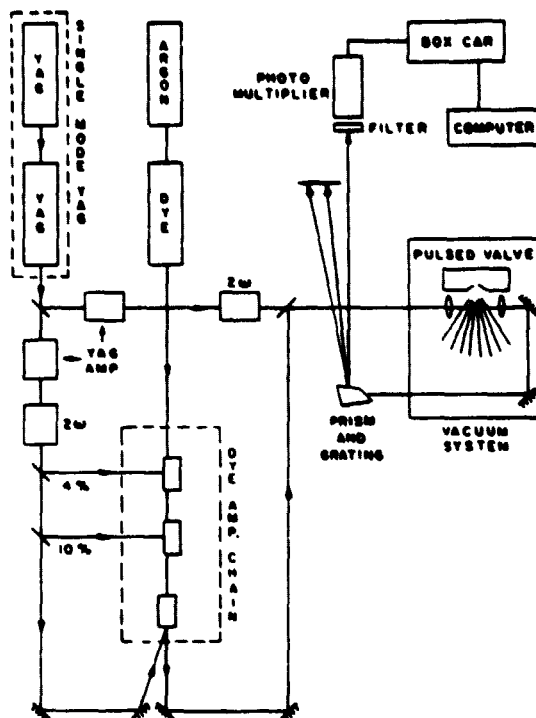


Fig. 1. Experimental apparatus for pulsed molecular beam CARS spectroscopy.

and an Nd:YAG pumped dye amplifier chain. The output of the Nd:YAG laser is split, amplified and frequency doubled to 532 nm. One green beam is used as the pump frequency in the CARS interaction. The second beam is used to pump a three-stage dye amplifier chain which amplifies a 100 mW single-frequency cw dye laser up to 0.5 MW peak power. The dye laser source is tuned to the Stokes frequency and combined collinearly with the pump beam. Both are focused tightly into the central region of an expanding molecular beam. The molecular beam is pulsed in synchronism with the 10 Hz lasers and produces a 100 μ s long burst of collisionally cooled molecules of $\approx 10^{16}$ mol/cm³ number density [11]. The signal produced at the anti-Stokes frequency is separated from the incident beams by prism and grating dispersing elements, filtered, and detected with a photomultiplier.

The tight focusing conditions and high peak powers of the interacting laser beams are responsible for saturation. In our case energies of 0.1 and 1.0 mJ in the

Stokes and pump beams respectively, are enough to significantly perturb the population difference ΔN . Fig. 2 shows a sequence of spectral scans of the ν_2 Q-branch of acetylene at successively higher pump energies. The 3:1 odd:even nuclear spin degeneracy factor for acetylene is enhanced to 9:1 by the CARS process. Fig. 2a shows the unperturbed spectrum with clearly resolved Q-branch lines. Fig. 2b shows significant broadening brought about by an increase in pump energy to 2 mJ. Along with the broadening there is a change in relative intensities between different lines. Fig. 2c shows strong saturation broadening at 4.5 mJ of pump energy. At this pump intensity $\approx 30\%$ of the population has been induced to the upper level.

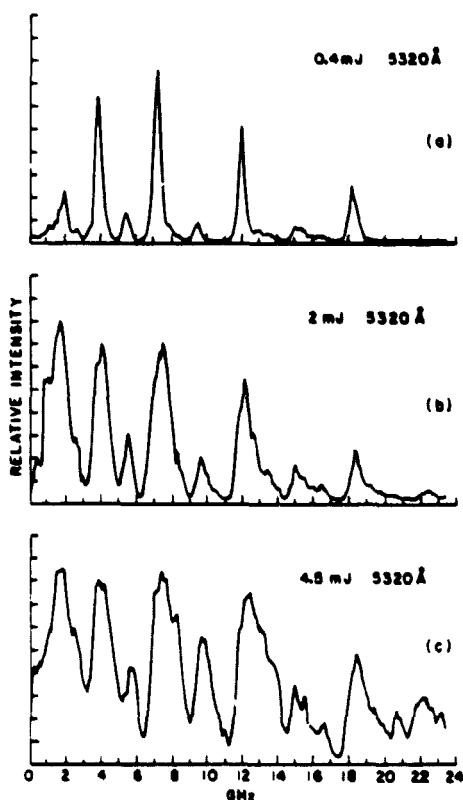


Fig. 2. CARS spectra of the ν_2 Q-branch of acetylene. (a) Unperturbed spectrum at 0.4 mJ 5320 Å energy. (b) same spectrum with 2 mJ 5320 Å energy. (c) same spectrum with 4.5 mJ 5320 Å energy. In all spectra the Stokes energy at 5944 Å was kept at 0.1 mJ energy.

The ac Stark effect is another line broadening mechanism which occurs at very high laser intensities. Recently Rahn et al. [12] presented a classical theoretical treatment of ac Stark broadening along with experimental results for the CARS interaction. Using the acetylene molecular constants we calculate an ac Stark broadening for acetylene of 3.5 MHz/GW cm^2 . Using the measured value of intensity of 35 GW/ cm^2 , at 2 mJ input energy for the present CARS experiment, we obtain less than 100 MHz for Stark broadening. Comparing this to the measured saturation broadening at 0.1 mJ Stokes and 2 mJ pump energies of 1050 MHz and the calculated broadening using eq. (5) of 1150 MHz, we see that ac Stark broadening plays a small role in the observed spectral broadening. To verify this, we lowered the Stokes energy below 0.1 mJ while keeping the pump energy constant and observed a decrease in the broadening. This is to be expected for saturation broadening which is dependent on the product $I_p I_s$, but is not to be expected for Stark broadening, which depends on the sum of intensities.

In conclusion we have observed line broadening due to population saturation in high-resolution coherent Raman spectroscopy of C_2H_2 in a pulsed supersonic molecular beam source. Saturation broadening sets another limit on the ultimate sensitivity and resolution of coherent Raman spectroscopic techniques. However, it also offers the possibility of new measurement techniques based on the induced population shifts.

We want to acknowledge the support of this work by the National Science Foundation under Grant no. CHE 791-12673 and by the National Aeronautics and Space Administration under Grant no. NSG 2372. Friederich König would like to acknowledge the support of the Max Kade Foundation. Peter Oesterlin wishes to thank the Deutsche Forschungsgemeinschaft for support.

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PULSED AND CW MOLECULAR BEAM
CARS SPECTROSCOPYR.L. Byer, M. Duncan¹, E. Gustafson
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The advantages of molecular beam Coherent Anti-Stokes Raman Spectroscopy include increased spectral resolution from sub-doppler linewidths, improved signal-to-noise resulting from spectral simplification due to rotational cooling upon expansion, and the possibility of studying molecular complexes generated by the expansion process. In this paper we report recent high resolution CARS studies using pulsed laser sources combined with a reliable pulsed molecular beam source and the first cw CARS measurements in a steady state high Mach number supersonic expansion.

High resolution pulsed molecular beam CARS measurements of the Q-branch of acetylene were used to characterize the properties of the pulsed molecular beam expansion. The onset of saturation broadening in a Raman spectrum was observed for the first time in the resolved Q-branch spectrum of expansion cooled acetylene. The previously unresolved ν_2 Q-branch of ethylene was resolved in the expansion cooled spectrum.

We have obtained the first high resolution cw CARS spectra of the CH_4 Q-branch in a steady state supersonic expansion. The supersonic jet expansion is a very useful spectroscopic tool that provides a convenient method of generating a range of molecular temperatures and densities. We observed, and have included in the CARS lineshape theory, the effects of transit time broadening evident in the tightly focused geometry used to obtain the supersonic jet CARS spectra of CH_4 .

2. Pulsed Molecular Beam CARS

The possibility of high resolution CARS spectroscopy in a supersonic molecular beam was theoretically analyzed by DUNCAN and BYER [1] in 1979. Initial estimates of the required laser power and resulting signal-to-noise ratios showed that conventional effusive molecular beam sources could not be used in the proposed measurements because of their inherently low molecular density. The molecular beam CARS experiment was, therefore, designed to utilize the pulsed nozzle source introduced by GENTRY and GIESE [2]. Simultaneously with the development of a 10 Hz, reliable, pulsed nozzle [3] a high peak power, single axial mode, unstable resonator

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Nd:YAG source was successfully demonstrated using injection locking techniques [4]. A Nd:YAG pumped dye amplifier chain was also implemented to provide high peak power amplified output from a cw dye laser source. The doubled Nd:YAG source and the dye laser source both operated at their Fourier transform linewidth limits near 100 MHz. The laser sources are described in more detail in [6]. Figure 1 shows a schematic of pulsed molecular beam CARS apparatus.

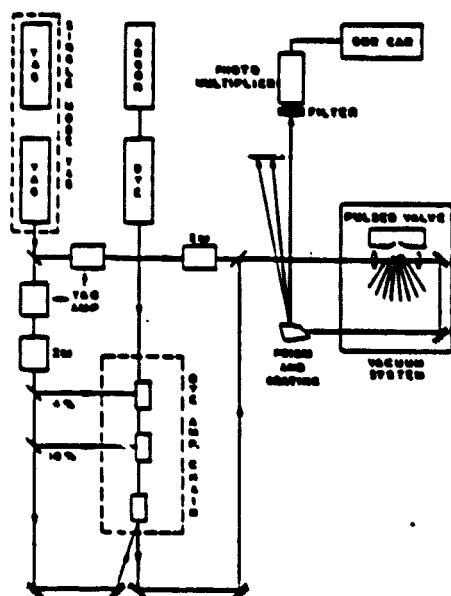


Fig. 1. Experimental arrangement for recording pulsed supersonic molecular-beam CARS spectra.

During the construction of our pulsed molecular beam CARS apparatus shown in Fig. 1, low resolution CARS of a continuous nitrogen supersonic flow was demonstrated by HUBER-WALCHLI, GUTHALS and NIBLER [7], early results of cw CARS of CH₄ in a supersonic jet were reported [8] and a series of high resolution Raman Gain Spectroscopy measurements of CH₄ followed by other molecules were obtained by VALENTINI, ESHERICK and OWYOUNG. [9]

The principal advantage of the supersonic molecular beam in these experiments is the spectral simplification provided by the reduced rotational temperature. The temperature for a continuum expansion in a supersonic jet is given by [10]

$$T = T_0 / [1 + \frac{1}{2}(\gamma - 1)M^2], \quad (1)$$

where

$$M = A \left(\frac{X - X_0}{D} \right)^{\gamma-1} - \frac{1}{2} \frac{(\gamma + 1)}{(\gamma - 1)} \left[A \left(\frac{X - X_0}{D} \right)^{\gamma-1} - 1 \right] \quad (2)$$

is the Mach number, γ is the ratio of specific heats, A is a constant determined by γ , X is the distance from the nozzle and D is the nozzle diameter.

We have used CARS spectra of the ν_2 Q-branch of acetylene where $\gamma = 7/5$ to verify the expansion cooling provided by the pulsed nozzle. The measurements showed that during the steady state expansion phase of the 100 μ sec long gas pulse emitted by the nozzle (1) is indeed obeyed when dimer formation is not significant at low gas densities. At higher gas densities dimer formation, with the resultant heat release [11], prevents cooling to the theoretically predicted temperatures. Figure 2 shows the Q-branch spectra of acetylene obtained in a static cell, at 80°K and at 20°K expansion temperatures. Figure 3 shows the rotational temperature in the supersonic expansion vs X/D . Dimer formation clearly prevents acetylene from reaching predicted temperatures except at low gas density or when seeded in helium.

The spectral simplification provided by the supersonic expansion is illustrated by the ν_2 Q-branch of ethylene. Figure 4 shows the spectrum at room temperature in a static cell at 60 torr pressure.

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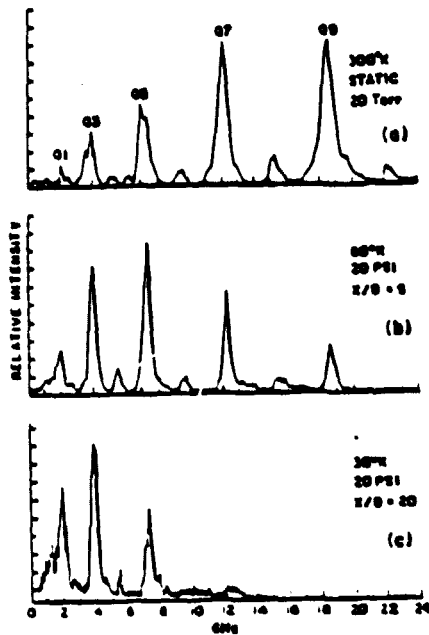


FIG. 2--Spectra of the v_2 Q-branch of acetylene taken with the CARS technique in (a) static gas (b) in the molecular beam at $X/D = 5$ and (c) in the molecular beam at $X/D = 20$.

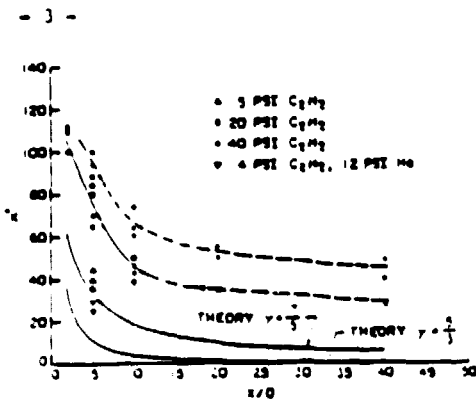


FIG. 3--Plot of rotational temperature in the supersonic expansion vs X/D . Theoretical curves for gases with $\gamma = 7/5$ and $\gamma = 5/3$ are shown.

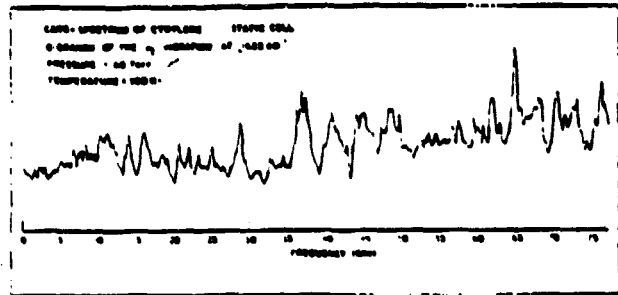


FIG. 4--CARS spectrum of the v_2 Q-branch of ethylene at 60 torr in a static cell.

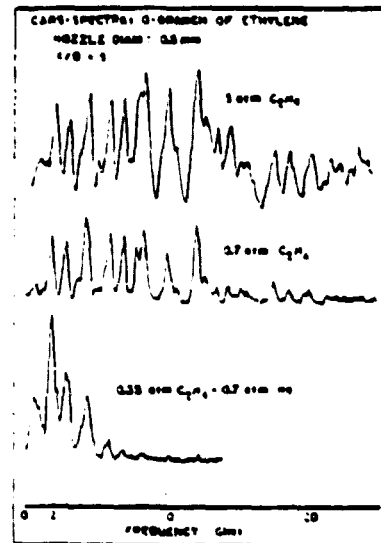


FIG. 5--CARS spectra of the v_2 Q-branch of ethylene at $X/D = 5$ at various input pressures and seeded in helium.

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Figure 5 shows the same spectrum at successively colder locations along the jet expansion. The temperatures indicated in the figure are estimates based on the known rotational constant for ethylene and a best fit to the envelope of the rotational component amplitudes. Efforts are under way to fit the spectrum and to determine more precise ethylene spectral constants.

The above molecular beam CARS spectra were generated with input pulse

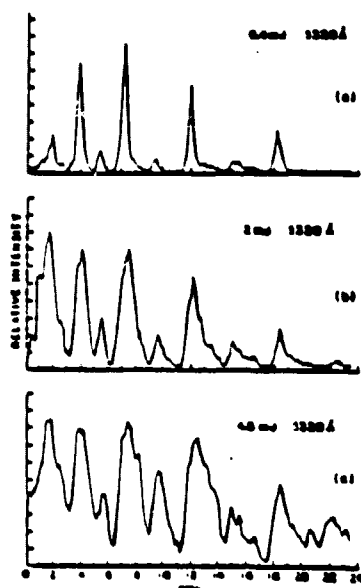


FIG. 6—CARS spectra of the v_2 Q-branch of acetylene.
a) unperturbed spectrum at .4 mJ 5320 Å energy b) at 2.5 mJ
c) same spectrum with 4.5 mJ 5320 Å energy. In all spectra the Stokes energy at 5944 Å was kept at .1 mJ.

energies of less than 1 mJ. Higher input energies near 5 mJ lead to saturation broadening of the Raman spectrum. The population changes induced by stimulated Raman scattering lead in turn to significant spectral broadening. We have observed saturation broadening in the expansion cooled acetylene spectra as shown in Fig. 6. [12]. Saturation broadening sets a limit to the sensitivity of the CARS process in high resolution studies. Improvements in sensitivity can be gained by decreasing the incident laser power in the interaction focal volume by either increasing the focal spot size or by increasing the pump and probe laser pulse widths. The latter option is desirable as it also leads to improved Fourier transform limited laser linewidths. However, longer pulse lengths are not easily achieved under normal Q-switched laser operation.

The early onset of saturation in the molecular beam Raman spectrum of acetylene suggests that Raman saturation spectroscopy, in the form first demonstrated by OWYOUNG and

ESHERICK [13], is a practical approach for sub-Doppler Raman spectroscopy. The shift of substantial population into the Raman level also suggests the possibility of state selective collisional transfer studies. Step wise ionization from the Raman level followed by detection of the ion or Raman ionization spectroscopy, is also possible.

There is interest in obtaining the Raman spectra of van der Waals complexes for the determination of the structure of these systems. The formation of complexes in the pulsed molecular beam expansion led us to search for a Raman signal due to ethylene complexes. Early results were encouraging in that a broad peak shifted 4.8 cm^{-1} from the previously resolved v_2 Q-branch peak of ethylene was observed. The magnitude of the peak varied with input pressure squared indicating either an ethylene complex or

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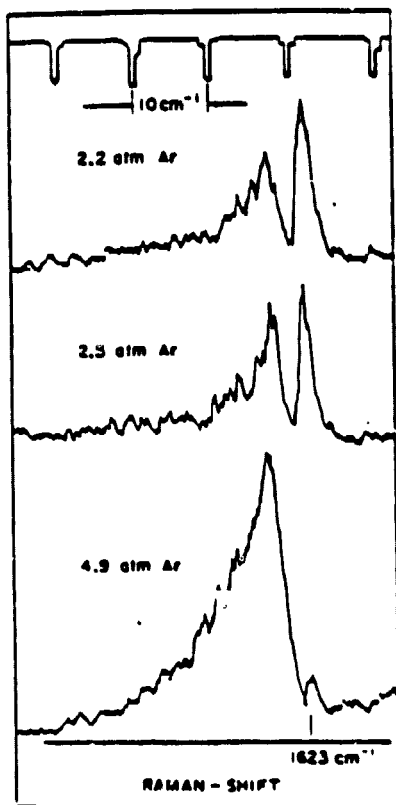


FIG. 7—CARS spectra of a supersonic molecular beam of an ethylene/argon mixture. The ethylene pressure was constant for all measurements, (0.27 atm.). The peak at 1623 cm^{-1} is the unresolved Q-branch of the ν_2 vibration of C_2H_4 . The peak at a smaller Raman shift is due to the ethylene molecular complex.

ethylene/argon complex was present. Figure 7 shows the CARS spectrum taken at 1 cm^{-1} resolution. The peak at 1623 cm^{-1} is the previously resolved (see Fig. 5), ν_2 Q-branch of ethylene. Measurements vs position from the nozzle showed that the complex began forming at $X/D = 5$, the signal strength increased to $X/D = 10$ and then decreased due to the decrease in density with further expansion.

Spectral scans attempted at higher resolution did not resolve structure in the spectrum but instead led to a significant decrease in signal strength that was suggestive of pre-dissociation of the complex. These results are preliminary and must be confirmed by further measurements.

Our pulsed molecular beam CARS system has now operated reliably for more than one year. Contrary to early expectations, measurements at good signal-to-noise with less than 1 mJ of input energy have been readily achieved. The combination of the single axial mode pulsed laser sources and the reliable pulsed nozzle have allowed significant advances to be made in high resolution Raman spectroscopy.

3. cw Supersonic Jet CARS

Supersonic cooling in steady state flows can be achieved in the laboratory using available vacuum pumps if the nozzle diameter is less than approximately 1 mm. We have constructed a 4 mm diameter supersonic jet backed by an old nitrogen laser vacuum pump. The jet is enclosed in a 1 cm x 1 cm dye laser cuvette for easy optical access. Control of the back pressure and of the input pressure allows a wide range of Mach flows up to Mach 8 to be generated at minimum gas consumption. The supersonic jet was used in cw CARS studies of the flow density, temperature and velocity. The study showed that the supersonic jet is an inexpensive, straightforward method of generating molecular pressures from 1 atm to less than 1 torr with corresponding temperatures from room temperature to less than 200K under very well controlled conditions.

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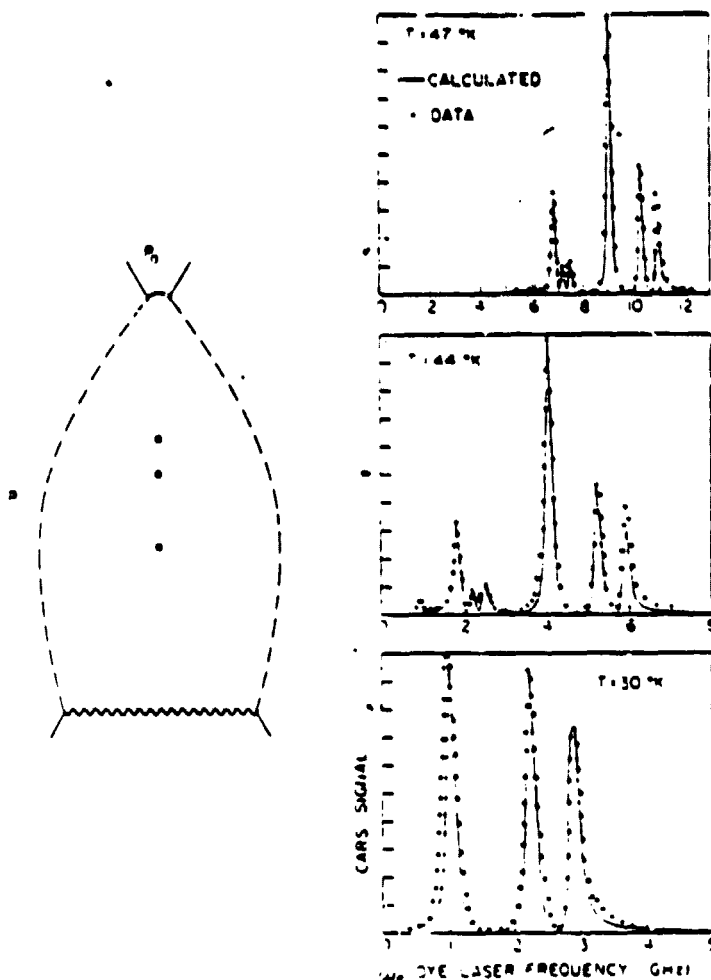


FIG. 8—Schematic of the supersonic jet expansion showing the location of the CARS measurements along the jet axis. The dashed line indicates the barrel shock and the wavy line the location of the Mach disk. cw CARS spectra of CH_4 Q-branch at the temperatures indicated. The dots are the data, the solid line the calculated spectra.

A schematic of the supersonic jet with spectra of the methane Q-branch taken at three positions along the expansion is shown in Fig. 8. The spectra were taken using the cw CARS apparatus described previously [14]. Spatial location in the supersonic jet was assured by using a tight focusing geometry with 3.7 cm focal length lenses providing a $2\text{ }\mu\text{m}$ spot size with 90% of the CARS signal generated in less than 100 μm length. It is interesting to note that less than 10^8 molecules were in the interaction volume of $6 \times 10^{-10}\text{ cm}^3$ at 10 torr pressure.

- 7 -

The spectral simplification of the methane Q-branch to the ground quantum state is illustrated in the $T = 300\text{K}$ spectrum of Fig. 8. Here the $J = 0, 1$ and 2 rotational components are fully resolved. The spectral resolution was set by residual Doppler broadening of 100 MHz , transit time broadening of 100 MHz , and laser linewidth jitter of 30 MHz . The theoretical fit to the data points was made using a CARS lineshape theory that included transit time broadening. The cw CARS spectrum was obtained using a 3W argon ion laser and 100 mW of cw dye laser input. Typical signal count rates were 1000 cps at pressures of a few torr. The signal levels were high due to the spectral simplification that resulted from the expansion cooling. Signal levels were high enough to allow an accurate measurement jet flow velocity and temperature.

These results illustrate the spectroscopic utility of a simple steady state supersonic jet. The independent control of input pressure and backing pressure coupled with position along the expansion axis of the jet allows ready access to a wide range of temperatures and pressures. The small diameter jet provides adequate interaction length for nonlinear spectroscopy and yet minimizes gas consumption at even high Mach number flows. For example, the present jet consumed approximately 1 bottle of methane for eight hours of operation.

4. Conclusion

We have demonstrated that high resolution Raman spectra of complex molecules can be obtained using a combination of pulsed high peak power single axial mode laser sources and a pulsed supersonic beam source. The pulsed nozzle reduces the vacuum pumping requirements by a factor of 10^4 so that even a small 6'' diameter diffusion pump provides adequate pumping. Spectral simplification due to expansion cooling allows the Raman spectra of even complex molecules to be resolved, improves the signal-to-noise level and introduces the possibility of Raman studies of molecular complexes formed by the expansion process. Saturation effects were observed. Improvements in both the pulsed laser sources and the pulsed nozzle should greatly enhance the ease of pulsed supersonic expansion spectroscopy.

Our investigation of the fluid flow properties of a steady state supersonic jet has shown that cw CARS is readily performed in this simplest of flows. The ease of construction and operation of the steady state supersonic jet should lead to its use in a much wider range of spectroscopic studies.

Acknowledgements

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COHERENT ANTI-STOKES RAMAN SCATTERING (CARS) OF LARGE C_2H_4 -Ar CLUSTERSF. KÖNIG ^{*}, P. OESTERLIN [‡] and R.L. BYER*Applied Physics Department, Stanford University, Stanford, California 94305, USA*

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CARS spectra from a supersonic molecular beam of ethylene/argon mixtures show a strong signal close to the Q branch of the ν_2 vibration of ethylene. The pressure dependence and scaling laws for a condensing molecular beam indicate that it is due to large C_2H_4 -Ar clusters. The experiment did not permit the identification of the clusters.

We report the first direct observation of the Raman spectra of molecular clusters using coherent anti-Stokes Raman spectroscopy (CARS) in a pulsed molecular beam. Such molecules have been the subject of increasing interest. Experiments investigating fluorescence [1], photoionization [2], and vibrational predissociation [3,4] have been performed, as well as several theoretical treatments [5,6]. There is interest in obtaining Raman spectra of molecular clusters for the determination of their structure. However, because they are normally generated in molecular beams, at low density, no direct observation using Raman spectroscopy has been reported.

We have carried out CARS spectroscopy using high peak power lasers in a pulsed molecular beam system [7,8]. For a molecular beam of ethylene/argon mixtures we have observed structure in the spectra which is caused by large molecular complexes of the type $(C_2H_4)_m Ar_n$. The measured Raman shift is ≈ 4.8 cm^{-1} less than the C_2H_4 Q-branch vibration at 1623 cm^{-1} . The present measurements to locate and detect the cluster spectrum were carried out at a low resolution ($\Delta\nu \approx 1.1$ cm^{-1}) so that the spectral feature appears as a broad peak.

The apparatus is described in more detail elsewhere [7]. It consists of an unstable resonator Nd:YAG

laser which is pulsed with a repetition rate of 10 Hz. Its output is amplified and frequency doubled to 532 nm. One part of this beam is used as the pump for the CARS process. The other part pumps a three-stage dye amplifier which amplifies the output of a cw dye laser and supplies the Stokes photons for the CARS interaction. Typical pulse energies and lengths are 12 mJ and 10 ns for the 532 nm beam and 2 mJ and 4 ns for the dye amplifier output at 582 nm. The bandwidths for the low-resolution study reported here are 0.8 cm^{-1} for both beams. The two laser beams are spatially overlapped and focused into a free-expansion molecular beam. The CARS signal, after separation from the laser beams by dispersing elements and filtering, is detected by a photomultiplier, processed in a boxcar integrator and plotted on a chart recorder. A simultaneous plot of the output of a 10 cm^{-1} free spectral range interferometer, which monitors the scanning dye laser, provides a relative frequency scale.

The molecular beam source is a pulsed nozzle which is described in detail in another paper [9]. It is synchronized with the pulsed laser system and supplies gas pulses of 100 μs length. The nozzle has a diameter of $D = 0.5$ mm. The spectra were taken at a normalized distance of $x/D = 7$ from the exit of the nozzle. The pressure of C_2H_4 was held constant at 0.27 atm and the pressure of Ar was varied between 1.4 and 4.9 atm during the measurements.

Fig. 1 shows three of the measured spectra with argon pressures of 2.2, 2.5 and 4.9 atm. The peak at a Raman shift of 1623 cm^{-1} is the unresolved Q

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branch of the ν_2 vibration of the C_2H_4 molecule. Its rotational structure has been recently resolved with our apparatus operating in the high-resolution mode [10]. The broader peak at smaller Raman shift is assigned to $(C_2H_4)_m Ar_n$ molecular complexes. The spacing between the two peaks is $4.8 \pm 1.1 \text{ cm}^{-1}$. The marks of the 10 cm^{-1} interferometer are shown on top of the spectra. The width of the interferometer peaks indicates the stepwidth of 0.8 cm^{-1} which is smaller than the resolution of 1.1 cm^{-1} .

The increase of the cluster peak integrated intensity with increasing Ar pressure can easily be seen in fig. 1. At 2.2 atm of argon, the signal intensities are approximately equal whereas at 4.9 atm argon pressure the signal from the $(C_2H_4)_m Ar_n$ molecule is more than 200 times larger than the C_2H_4 Q-branch signal. Although it is not possible to calculate the Raman shift of such a cluster because of the large number of particles and the unknown binding forces, we believe that the peak is due to a shift of the ν_2 vibration of C_2H_4 combined with low-frequency vibrations of van der Waals bonds. A similar shift was observed in high-pressure spontaneous Raman scattering of H_2 He and H_2 Ar collision complexes [11] as well as in low-pressure infrared absorption measurements in mixtures of H_2 with Ar, Kr and Xe [12].

An identification of the clusters was not possible for several reasons. First, the signal intensity was too low to carry out the measurements in the free molecular flow region of the beam. The spectra shown in fig. 1 were taken at a reduced nozzle distance of $x/D = 7$, where the collision rate in the beam is still high.

Secondly, it is not possible to measure the masses of large clusters accurately in a conventional mass spectrometer with electron impact ionization. Measurements with inert-gas clusters have shown that large clusters fragment strongly, even at electron energies just above the ionization threshold [13]. Therefore, a mass spectrometer tends to show a cluster distribution with too small a mean cluster size.

Despite the fact that it was not possible to measure the cluster mass distribution, we can give some estimates about the mean cluster size. From the spectra in fig. 1 it can be seen that the signal due to ethylene monomers at 1623 cm^{-1} decreases with increasing argon pressure, indicating a decreasing density. Since the partial pressure of C_2H_4 is the same for all measurements (0.27 atm), the monomer density in the

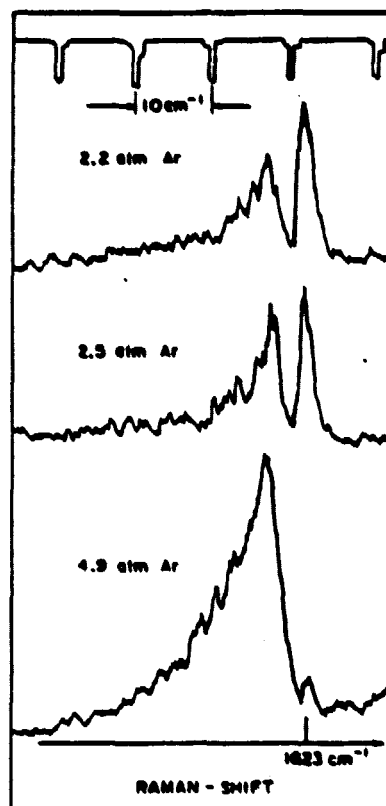


Fig. 1. CARS spectra of a supersonic molecular beam of an ethylene/argon mixture. The ethylene pressure was constant for all measurements (0.27 atm). The peak at 1623 cm^{-1} is the unresolved Q branch of the ν_2 vibration of C_2H_4 , the peak at a smaller Raman shift is due to $(C_2H_4)_m Ar_n$ clusters.

beam should be the same for a non-condensing beam. Its diminution is therefore caused by cluster formation. The spectra show that the monomer density decreases by approximately a factor of two when the argon pressure is increased from 2.2 to 4.9 atm (the peak height is proportional to the square of the density). Such a strong condensation, where $\approx 50\%$ of the particles in the beam are involved, certainly leads to the formation of large clusters.

For large distances from the nozzle, far away from the condensation region, the mean cluster size can be estimated from scaling laws. It depends mainly on two parameters, the product of stagnation pressure and nozzle diameter, pD , and the binding energy of the constituents of the cluster. In our experiment $pD =$

196 Torr cm for the highest pressure. The binding energy between two ethylene molecules is 18 meV [14] and between two Ar atoms 11 meV [15]. The binding energy between an Ar atom and an ethylene molecule is not known, but it is certainly of the same order of magnitude. With an average binding energy of 15 meV between two particles in the cluster we calculated a mean cluster size of ≈ 3500 atoms and molecules, using the scaling laws of Hagena [16]. For clusters of this size formed in a gas mixture of C_2H_4 and Ar it is reasonable to assume that they consist of both species.

Since our measurements were performed in the collision region of the beam, the scaling laws can give only an upper limit for the cluster size. The estimation of a lower limit is more difficult. The dimer concentration in strongly condensing beams has normally a maximum very close to the nozzle, at $x/D \approx 2$. Further downstream small clusters coagulate to larger complexes, so that at $x/D = 7$, where our experiment probed the beam, the mean cluster size is already large, about several hundred particles. This assumption is supported by the fact that for distances larger than 9 nozzle diameters the cluster signal in our experiment dropped rapidly, indicating that the formation of clusters stops at this distance, but their number density decreases due to the diverging gas beam. This justifies the assignment of the signal in our CARS spectra to clusters of the type $(C_2H_4)_m Ar_n$ with m and n between 100 and 1000.

With the assumption of many C_2H_4 molecules in a cluster, the surprisingly strong signal at 1618 cm^{-1} can be explained. In such a complex the density of particles is the same as in a liquid. Since the signal intensity for the CARS process depends on the squared density, only a few percent of clusters in the gas beam are necessary to give the signal ratio of 200 for the cluster signal to pure ethylene signal, as was observed in the measurement at the highest Ar pressure.

The tightly focused laser beams used in the CARS interaction permit the investigation of the density of van der Waals molecules at different distances from the nozzle. For example, for a mixture of 0.27 atm C_2H_4 with 2.2 atm Ar we observed that the CARS signal due to the complexes increases strongly from $x/D = 5-7$, indicating that these molecules are formed mostly at this distance from the nozzle. Measurements like this open the possibility to study the formation process of clusters in molecular beams.

Attempts to resolve any structure of the cluster signal failed because the signal intensity decreased strongly with increasing resolution (decreasing bandwidth of the lasers). This decrease in signal is explained by the large linewidth of the Raman resonance of the cluster, which in this case is $\geq 1\text{ cm}^{-1}$. We do not have a reliable model to describe this width, but there are many line-broadening effects in large clusters, e.g. combinations of the ν_2 vibration of ethylene with van der Waals vibrations, vibrational predissociation [17] or distribution of the C_2H_4 vibrational energy over many van der Waals bonds [18].

In conclusion we observed a strong additional peak in a CARS spectrum close to the Q branch of the ν_2 vibration of ethylene in a molecular beam of ethylene/argon mixtures. It is certainly due to large C_2H_4 Ar clusters. The measured linewidth of $\geq 1\text{ cm}^{-1}$ is explained by the interactions of the particles in the cluster which behaves like a liquid. The experiment did not give much information about the clusters themselves, mostly because we obtained a measurable signal only with a strongly condensing beam which contains large clusters of unknown composition. But improvements in sensitivity and signal-to-noise ratio should be possible in the future, for CARS as well as for other Raman techniques, making Raman spectroscopy a useful method for the investigation of molecular clusters.

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HIGH RESOLUTION cw CARS SPECTROSCOPY
IN A SUPERSONIC JET

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ABSTRACT

We have obtained high resolution cw CARS spectra of the ν_1 Q-branch of Methane in an underexpanded supersonic jet at temperatures as low as 31.5 K and pressures below 2 torr.

HIGH RESOLUTION cw CARS SPECTROSCOPY IN A SUPERSONIC JET

E.K. Gustafson, J.C. McDaniel and R.L. Byer

In this letter we report the first high resolution cw CARS spectroscopic measurements in a steady state supersonic jet. The advantages of CARS measurements in the jet over Raman spectroscopy in a static cell include spectral simplification due to rotational cooling upon expansion, reduced Doppler width, access to a wide range of temperatures and pressures in the jet flow, and improved signal-to-noise. In addition we have observed significant transit time broadening as a result of the tight focussing geometry used in the present experiment.

Molecular beam CARS spectroscopy was first proposed and analyzed by Duncan and Byer in 1979.¹ Recently coherent anti-Stokes Raman spectroscopy at low spectral resolution was demonstrated in a N_2 molecular beam by Huber-Walchli et.al.,² and at high resolution by Duncan et.al.,³ and Byer and Duncan.⁴ Raman gain spectroscopy of methane has been achieved in a molecular beam by Valentini et.al.⁵ The above experiments used high peak power laser sources to overcome the low signal levels which resulted from the low gas densities encountered in molecular beam sources. Resolutions were limited to approximately 100 MHz by the Fourier transform limited linewidths of the single axial mode pulsed laser sources.

In contrast to the above experiments, we report high resolution cw CARS measurements in a steady state supersonic free expansion jet. The jet offers the advantages of simple construction, high molecular density, and substantial

cooling in the isentropic expansion zone. The ability to use cw laser sources offers the potential of substantially higher resolution Raman spectroscopy than possible with high peak power lasers. In the present experiment, the linewidth is limited by a combination of residual Doppler broadening, transit time broadening and laser linewidth jitter.

Figure 1 shows a schematic of the cw jet CARS experiment. The pump beam is provided by a 4 watt single axial mode argon ion laser with a measured bandwidth of 30 MHz. The tunable source is a 599-21 Coherent Radiation dye laser, and has a 3 MHz bandwidth. Both laser beams are expanded, combined with a dichroic mirror, and then focussed with a 3.7 cm lens. The laser spot sizes were measured using a mechanical chopper and found to be approximately 10 microns, but the best fit to the experimental data was produced with spot sizes of 12 microns for the pump and 13.5 microns for the dye source. Care was taken to match the focal planes of the beams and to center the beam waists into the coldest part of the supersonic expansion. The generated anti-Stokes beam was collimated with a second 3.7 cm lens and spectrally dispersed from the pump and dye beams by a prism and grating, prior to the photon counting photomultiplier tube. The computer controlled the dye laser wavelength and recorded the spectrum. In Fig. 2 an expanded view of the supersonic jet and several spectra are shown. The cooling of the gas as it accelerates away from the nozzle is evident from the preferential population of the lower J levels.

The supersonic jet consisted of a $\frac{1}{2}$ mm diameter orifice centered in a 1 cm x 1 cm glass dye laser cuvette. The jet and surrounding cuvette were mounted on an x,y,z stage to allow easy access to various locations along

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Fig. 1
SUPERSONIC JET CARS EXPERIMENT

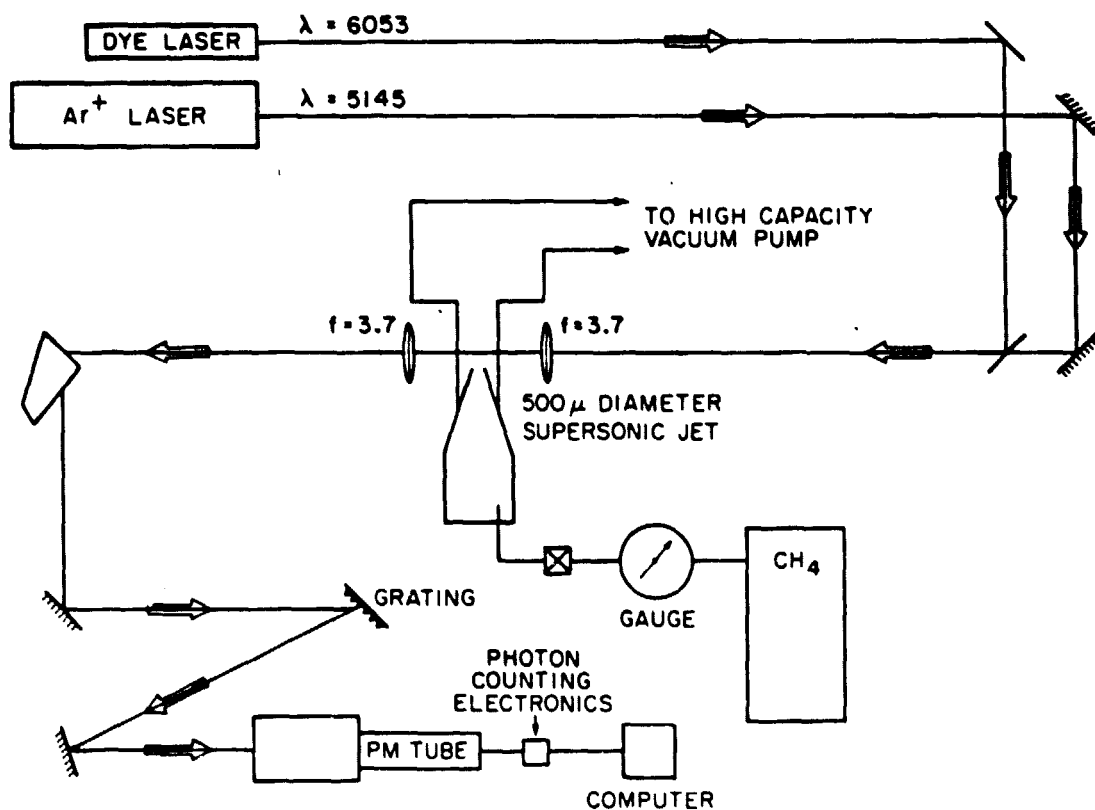


FIGURE 1--Supersonic jet CARS experimental arrangement

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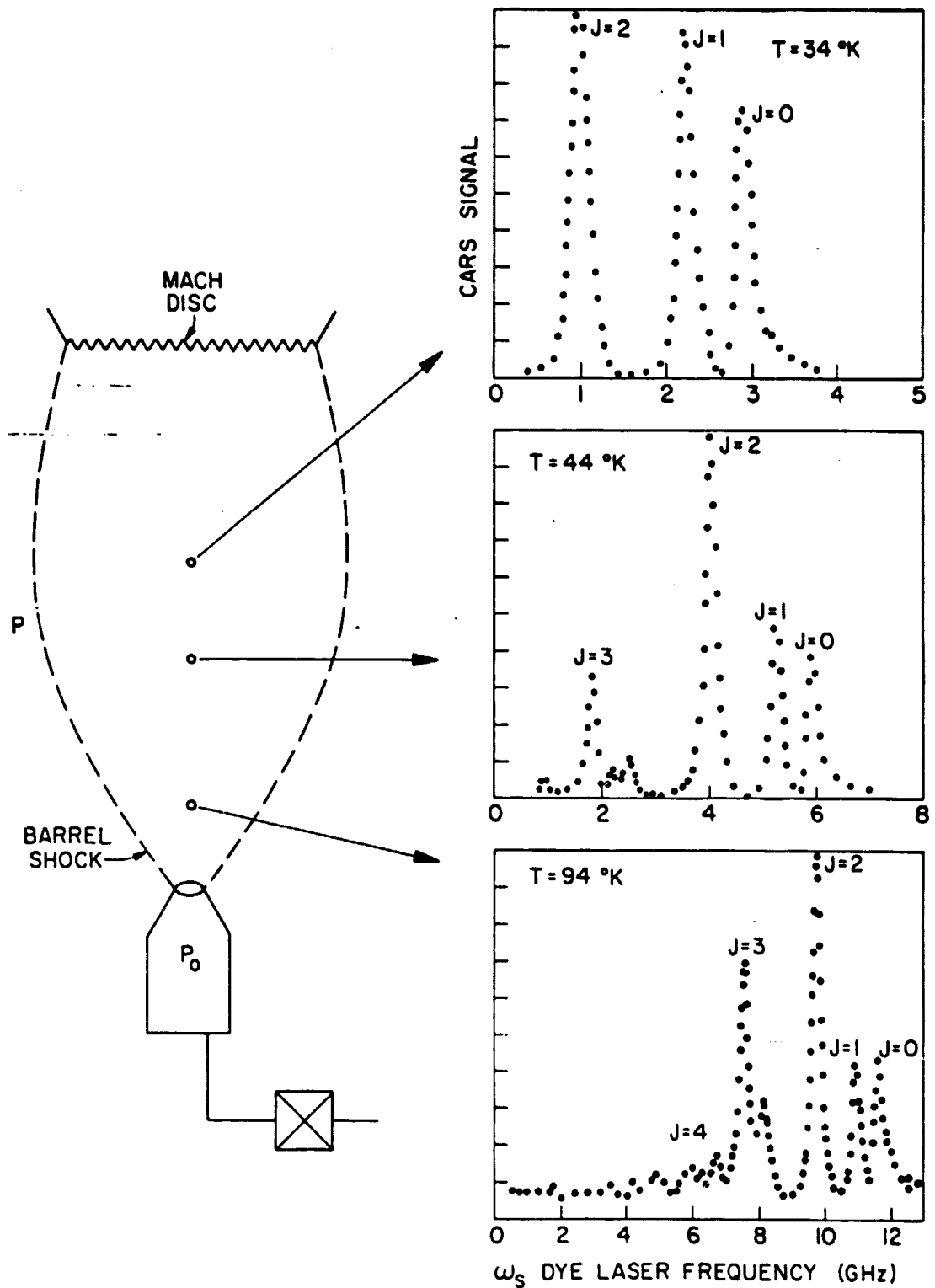


FIGURE 2--Supersonic jet and several spectra of the ν_1 Q-branch of Methane showing the cooling in the expansion region of the flow

the axis of the expansion. In this way regions from high temperatures to low temperatures could be accessed by physically moving the jet. The input pressure was controlled by adjusting the regulator on a standard gas bottle. The jet exhaust pressure was controlled through a throttle valve which was backed by a pump that provided approximately 10 CFM pumping speed. Typical operating pressures were 150 PSI input pressure and 30 - 250 torr backing pressure. The gas bottle provided up to eight hours of operation under these conditions. Mach numbers of up to 8.2 could be obtained just prior to the Mach disc shock front with a corresponding temperature of 24K and pressure of less than 0.5 torr. Pressure broadening of spectra taken under these conditions was negligible.

To ensure that the anti-Stokes signal was generated primarily in the coldest part of the flow it was necessary to focus tightly. In this tight focussing geometry transit time broadening became a significant broadening mechanism. Formally, the linewidth broadening effects were calculated by solving for the anti-Stokes field using a Green's function formalism and including the time dependence of the molecular positions across the Gaussian intensity pump and dye laser beams in the nonlinear driving polarization.

The power spectral density must be numerically evaluated and is

$$I(\nu) \propto \left| \int_{-\infty}^{+\infty} d\alpha \chi^{(3)}(\nu + \alpha) K(\alpha, w_{po}, w_{so}, \nu) \right|^2 \quad (1)$$

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where the kernel function $K(\alpha, w_{po}, w_{so}, v)$ is given by

$$K(\alpha, w_{po}, w_{so}, v) = \left(\exp - \left[\tau_s^2 + \left(\frac{t_p}{2} \right)^2 \right] \alpha^2 \right) \int_{-\infty}^{+\infty} dz R(z, w_{po}, w_{so}) \exp \left[\frac{\tau_s^2 \tau_D^4 + (2\tau_D^2 A_D A_s - \tau_s^2 A_s^2) z^2}{\tau_s^4 + A_D^2 z^2} \right] \alpha^2 \quad (2)$$

$$\times \exp i \left\{ \left[A_D + \left(\frac{t_p}{2} \right)^2 \frac{1}{z_p} \right] z + \frac{(\tau_s^4 A_D - 2\tau_s^2 \tau_D^2 A_s) z - A_D A_s^2 z^3}{\tau_s^4 + A_D^2 z^2} \right\} \alpha^2$$

where

$$t_p = \frac{w_{po}}{v} \quad \text{and} \quad t_s = \frac{w_{so}}{v} \quad \text{are the pump and Stokes transit times,}$$

$$\tau_s^2 = \left(\frac{t_p}{4} \right)^2 + \left(\frac{t_s}{4} \right)^2 \quad \text{and} \quad \tau_D^2 = \left(\frac{t_p}{4} \right)^2 - \left(\frac{t_s}{4} \right)^2 \quad \text{are related times and}$$

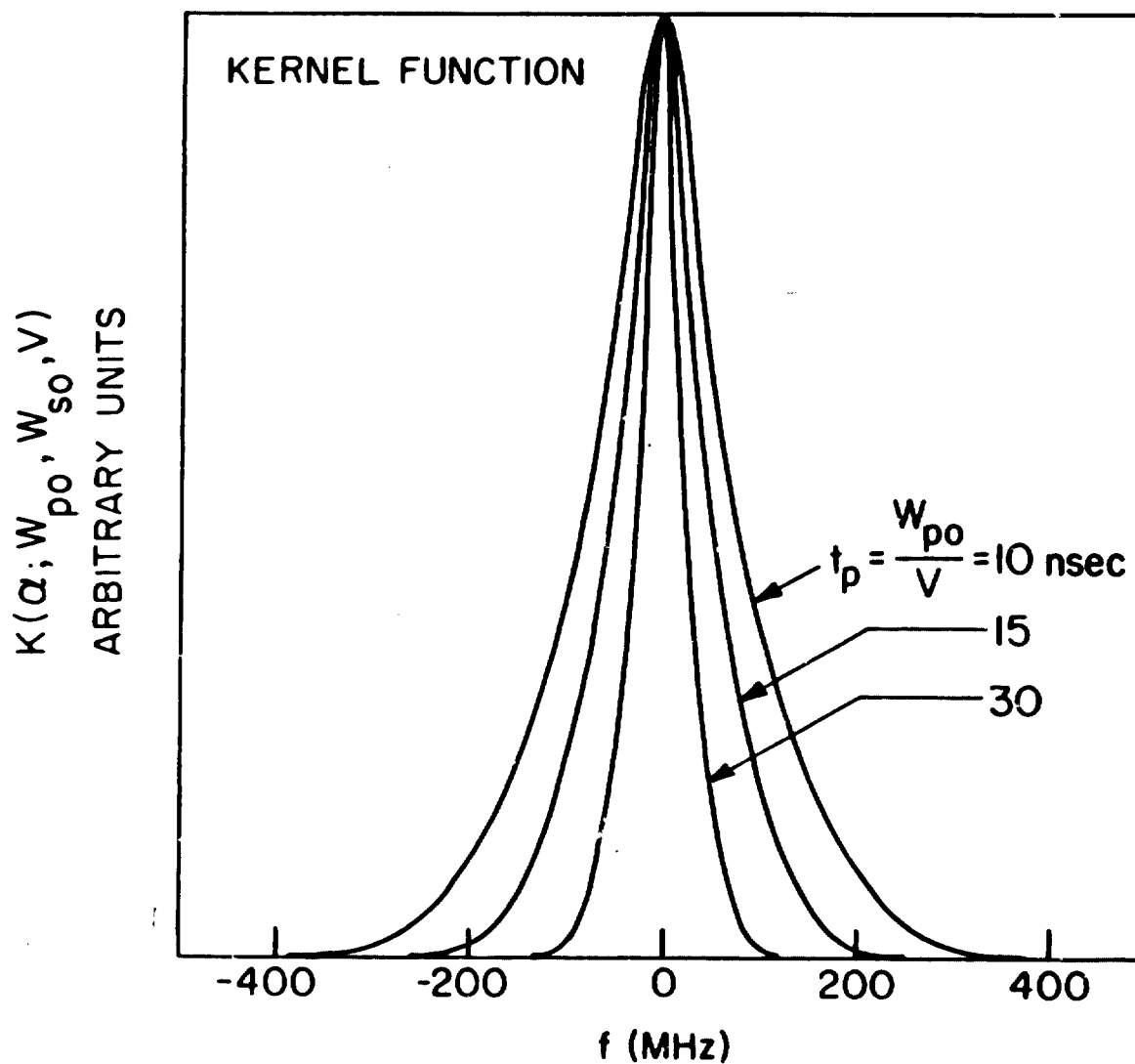
$$A_s = \left(\frac{t_p}{4} \right)^2 \frac{1}{z_p} + \left(\frac{t_s}{4} \right)^2 \frac{1}{z_s} \quad \text{and} \quad A_D = \left(\frac{t_p}{4} \right)^2 \frac{1}{z_p} - \left(\frac{t_s}{4} \right)^2 \frac{1}{z_s} \quad \text{are constants}$$

written in terms of the pump and Stokes beam Rayleigh ranges, z_p and z_s . The factor $R(z, w_{po}, w_{so})$ contains Gaussian beam parameters with w_{po} and w_{so} being the pump and Stokes beam spot sizes at the focus.

Here $\chi^{(3)}(\nu)$ is the third order susceptibility including Doppler broadening, α is the frequency variable of integration, v is the molecular flow velocity, and ν is the CARS frequency variable.

Figure 3 shows a computer generated plot of the kernel function $K(\alpha)$ for several different spot sizes. As the spot size decreases the effect of transit time broadening increases and the linewidth increases. In our experiment the linewidth due solely to transit time broadening is 114 MHz. In the limit of zero transit time broadening the total lineshape theory including Doppler broadening, pressure broadening, and transit time broadening reduces to the lineshape theory of Henesian and Byer.⁶

Figure 4 shows a spectrum taken of the ν_1 Q-branch of methane in a Mach 6.8 jet at a temperature of 34 K. The temperature was determined by the isentropic expansion relations for the supersonic flow. At the higher temperatures the higher rotational J values are populated although not nearly to the extent evident in previously published spectra of the ν_1 Q-branch of methane, taken at room temperature.⁷ As the temperature decreased, the spectrum simplified to include only the lower rotational components $J = 0$ to $J = 2$. The three nuclear spin components, A, E and F, remain at room temperature equilibrium ratios of 1:3:5 during the expansion. The measured linewidth for $J = 0$ is 204 MHz. The equivalent pressure is less than 2 torr. It is interesting to note that in the interaction volume, of less than 10^{-8} cm^{-3} , the net number of molecules contributing to the CARS signal is less than 3×10^9 for a single rotational component.



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FIGURE 3--Several transit time broadening kernel functions

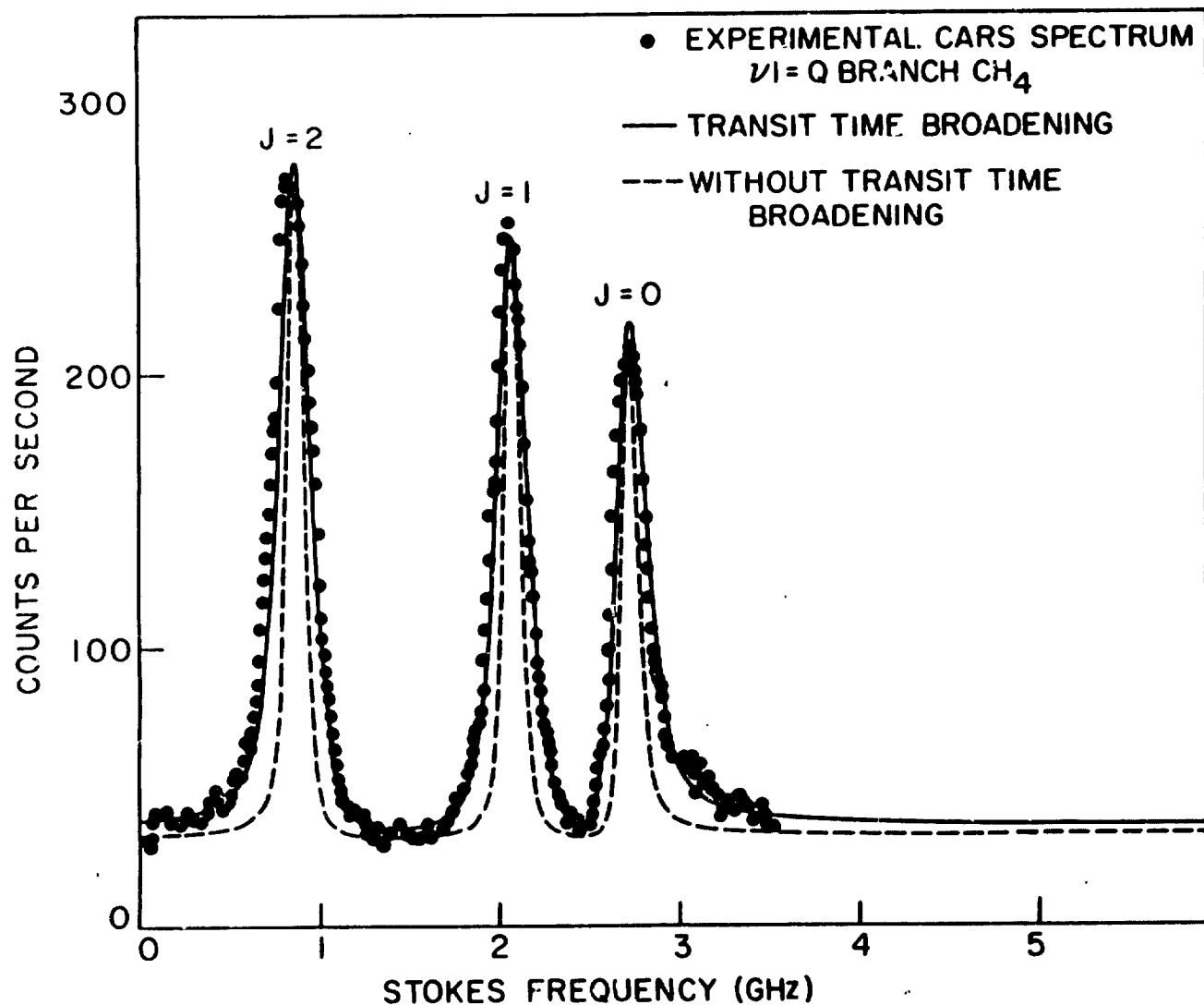


Figure 4--CARS theory including transit time broadening (solid lines), CARS lineshape theory without transit time broadening (dashed line), and experimental data (dots).

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The experimental spectra (dots) shown in Fig. 4 are well fit by the calculated theoretical spectra, including transit time broadening (solid lines). The dashed curve in Fig. 4 is the lineshape excluding transit time broadening. The lineshape theory thus included contributions from Doppler broadening, 10 MHz of pressure broadening and transit time broadening. The pressure and velocity used to evaluate the lineshape integrals were calculated for the jet using the theory of Ashkanas and Sherman.⁸ A temperature of 31.5 K produced the best fit to the data.⁹ In our present tight focusing geometry transit time broadening was comparable to the residual Doppler broadening of about 100 MHz.

The calculated linewidths and peak heights agree well with the measured values except for the $J = 2$ peak. In the linewidth calculations we assumed that the A & E nuclear spin components are degenerate for the $J = 2$ rotational level. The measured linewidth is 25 MHz wider than the linewidth of the $J = 0$ and $J = 1$ levels which suggests that the $J = 2$ nuclear spin components are not degenerate but are split by approximately 25 MHz.

In conclusion, we have demonstrated high resolution cw CARS spectroscopy in a supersonic jet expansion. The jet provides a convenient method of obtaining molecular cooling at relatively high density. The high density and spectral simplification lead to improved signal-to-noise compared to CARS spectroscopy in either a static cell or in a molecular beam expansion. We have observed transit time broadening and have included it in a generalized CARS lineshape expression.

The ease of construction and the wide range of temperatures and densities accessible in a supersonic jet make it a generally useful tool for high resolution molecular spectroscopy.¹⁰

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