High-resolution continuous-wave coherent anti-Stokes Raman spectroscopy in a supersonic jet

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We have obtained high-resolution cw coherent anti-Stokes Raman 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.

In this Letter we report the first known high-resolution cw coherent anti-Stokes Raman spectroscopy (CARS) 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 that is due to rotational cooling on expansion, reduced Doppler width, access to a wide range of temperatures and pressures in the jet flow, and improved signal-to-noise ratio. In addition, we have observed significant transit-time broadening as a result of the tight-focusing geometry used in the present experiment.

Molecular-beam CARS was first proposed and analyzed by Duncan and Byer in 1979.[1] Recently, CARS 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 that 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 is a schematic of the cw jet CARS experiment. The pump beam is provided by a 4-W 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 focused with a 3.7-cm lens. The laser spot sizes were measured by using a mechanical chopper and found to be approximately 10 μm, but the best fit to the experimental data was produced with spot sizes of 12 μm for the pump and 13.5 μm 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 before 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 0.5-mm-diameter orifice centered in a 1-cm × 1-cm glass dye-laser cuvette. The jet and the surrounding cuvette were mounted on an x, y, z stage to permit easy access to various locations along the axis of the expansion. In this way regions from high temperatures to low temperatures were accessible 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 300 l/min pumping speed. Typical operating pressures were 68-kg/cm (150-psi) input pressure and 30–250-Torr backing pressure. The gas bottle provided up to 8 h of operation under these conditions. Mach numbers of up to 8.2 could be obtained just before the Mach disk

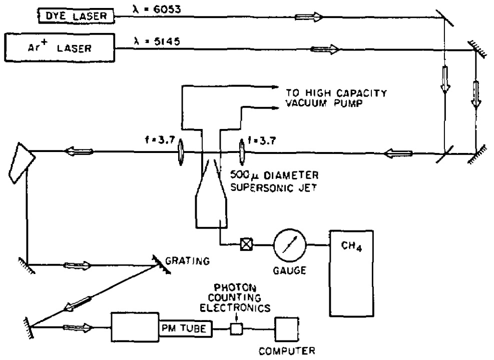

Fig. 1. Supersonic jet CARS experimental arrangement.

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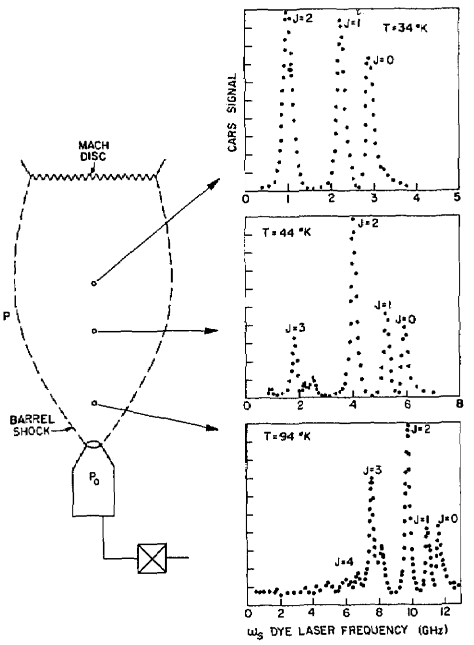

Fig. 2. Supersonic jet and several spectra of the ν_1 Q branch of methane showing the cooling in the expansion region of the flow.

shock front with a corresponding temperature of 24 K 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-focusing geometry, transit-time broadening became a significant broadening mechanism. Formally, the linewidth-broadening effects were calculated by solving for the anti-Stokes field by using a Green-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

$$I(\nu) \propto \left| \int_{-\infty}^{+\infty} \mathrm{d}\alpha \chi^{(3)}(\nu + \alpha) K(\alpha, w_{p0}, w_{s0}, v) \right|^2 , \quad (1)$$

where the kernel function $K(\alpha, w_{p0}, w_{s0}, v)$ is given by

$$\begin{aligned} K(\alpha, w_{p0}, w_{s0}, v) = {} & \left\{ \exp - \left[\tau_s{}^2 + \left(\frac{t_p}{2} \right)^2 \right] \alpha^2 \right\} \\ & \times \int_{-\infty}^{+\infty} \mathrm{d}z R(z, w_{p0}, w_{s0}) \\ & \times \exp \left[\frac{\tau_s{}^2 \tau_D{}^4 + (2\tau_D{}^2 A_D A_s - \tau_s{}^2 A_s{}^2) z^2}{\tau_s{}^4 + A_D{}^2 z^2} \right] \alpha^2 \\ & \times \exp i \left\{ \left[A_D + \left(\frac{t_p}{2} \right)^2 \frac{1}{z_p} \right] z \right. \\ & \left. + \frac{(\tau_s{}^4 A_D - 2\tau_s{}^2 \tau_D{}^2 A_s) z - A_D A_s{}^2 z^3}{\tau_s{}^4 + A_D{}^2 z^2} \right\} \alpha^2 , \end{aligned}$$

where $t_p = w_{p0}/v$ and $t_s = w_{s0}/v$ are the pump and Stokes transit times, $\tau_s{}^2 = (t_p/4)^2 + (t_s/4)^2$ and $\tau_D{}^2 = (t_p/4)^2 - (t_s/4)$ are related times, and $A_s = (t_p/4)^2(1/z_p) + (t_s/4)^2(1/z_s)$ and $A_D = (t_p/4)^2(1/z_p) - (t_s/4)^2(1/z_s)$ are constants written in terms of the pump- and Stokes-beam Rayleigh ranges, z_p and z_s. The factor $R(z, w_{p0}, w_{s0})$ contains Gaussian-beam parameters with w_{p0} and w_{s0} 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 kernal 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 that is due solely to transit-time broadening is 114 MHz. In the limit of zero-transit-time broadening, the total line-shape theory, including Doppler broadening, pressure broadening, and transit-time broadening, reduces to the line-shape 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

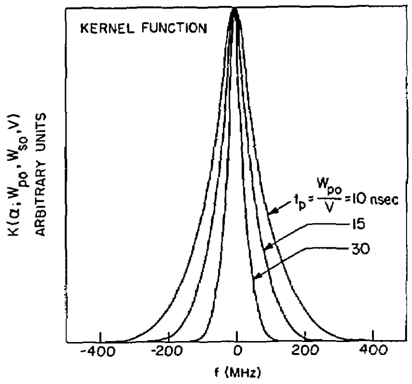

Fig. 3. Several transit-time-broadening kernel functions.

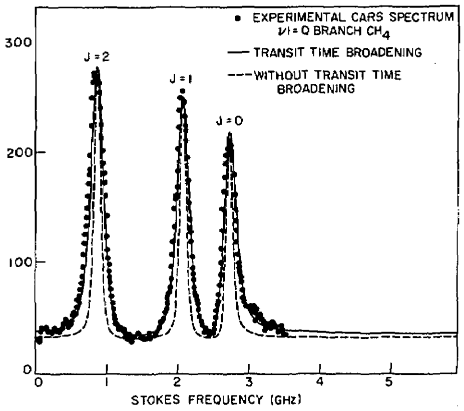

Fig. 4. CARS theory including transit-time broadening (solid lines), CARS line-shape theory without transit-time broadening (dashed line), and experimental data (dots).

populated, although not nearly to the extent evident in previously published spectra of the ν_1 Q branch of methane, taken at room temeprature.[7] As the temperature decreased, the spectrum simplified to include only the lower rotational components $J = 0$ to $J = 2$. 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^{10} for a single rotational component.

The experimental spectra (dots) shown in Fig. 4 are well fitted by the calculated theoretical spectra, including transit-time broadening (solid lines). The dashed curve in Fig. 4 is the line shape excluding transit-time broadening. The line-shape theory thus included contributions from Doppler broadening, 10 MHz of pressure broadening, and transit-time broadening. The pressure and velocity used to evaluate the line-shape integrals were calculated for the jet by 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 with 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 line width calculations we assumed that the F and 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 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 ratio compared with CARS in either a static cell or a molecular-beam expansion. We have observed transit-time broadening and have included it in a generalized CARS line-shape expression.

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

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