PLENARY LECTURE

PROC. XIIth INT. CONF. ON RAMAN SPECTROSCOPY
ED. BY J.R. DURIG, JOHN WILEY AND SONS, 1990

HIGH RESOLUTION COHERENT RAMAN SPECTROSCOPY


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One of the principal advantages of nonlinear coherent forms of Raman spectroscopy such as CARS (Coherent Anti-Stokes Raman Scattering) and SRS (Stimulated Raman Scattering) is the high resolution achievable using single frequency lasers. In contrast to spontaneous Raman spectroscopy, for sharp Raman transitions, such as occur in low pressure gases and cooled samples, the detection sensitivity increases as one seeks higher resolution. Both c.w. CARS and SRS experiments have been done with resolution of a few MHz, however pulsed lasers generally offer much greater detection capability while still providing resolution of the order of 100 MHz or better. In this lecture, some of the experimental aspects of the c.w. and pulsed measurements will be considered and then a range of applications will be discussed.

Schrötter et al. [1] have given a detailed discussion of the construction of a c.w. intracavity CARS spectrometer at Munich and pulsed CARS and SRS spectrometers at Dijon. The pulsed CARS system is remarkable in that it utilizes injection-locked flashlamp-pumped dye lasers with effective linewidths of 6 MHz. More common is the use of Nd:YAG pumped dye lasers where the Fourier transform of the short pulse typically gives a resolution of 75 to 150 MHz. Fig. 1 shows such a system in use at Oregon State University for SRS spectroscopy [2]. This consists of a Coherent 699-29 ring dye laser which is pulse-amplified by a single-mode Nd:YAG laser to give 1 to 15 mJ energy with a linewidth of about 90 MHz. This tunable source is mixed with various single-mode argon or krypton ion laser lines to provide Raman Loss or Gain signals in the latter probe beams when the frequency difference matches a rotational or vibrational-rotational resonance. In this setup complete coverage of the 0 to 4000 cm⁻¹ Raman shift region is possible with the use of the optimal Rhodamine 6G dye in the ring laser. A recent modification of this apparatus consists of the addition of another amplifier chain to increase the energy of the ion lasers to give a second, pulsed source for high resolution CARS measurements. For many purposes, CARS studies do not require such high resolution and a single-mode Nd:YAG laser can be combined with commercial pulsed dye lasers to give a resolution of 0.05 to 0.1 cm⁻¹ and a much simpler experimental apparatus.
Fig. 1. Schematic of the SRS apparatus at Oregon State University.

Because of their nonlinear power dependence, both CARS and SRS signals benefit from high input power densities. For CARS, the principal limitation is saturation broadening which is observable for $P_1 P_2$ power product densities in excess of about $30 \text{ GW}^2/\text{cm}^4$. This effect is not a problem for SRS due to the low probe power. However pulsed laser intensities in excess of 1-2 $\text{GW}/\text{cm}^2$ can produce observable ac Stark shifts and broadening. For pure rotational transitions, the M degeneracy of the rotational levels is split by the dc component of the field perturbation term $H = -\gamma E^2/4$, where $\gamma$ is the polarizability anisotropy of the molecule and $E$ is the pump laser field. The effect on the rotational levels is to cause splittings which are polarization dependent but observable only for low J transitions. Thus the effect is not too restrictive for high resolution rotational spectroscopy.

For vibrational Q branch studies, the ac Stark shifts are about the same for $v = 0$ and 1 levels so that the transition splittings are negligible. There is however a second effect, a shift in the vibrational frequency caused by the field acting through the polarizability derivative $(da/dR)$ [3]. SRS spectra recorded by Beck (Fig. 2) show the effect on the Q branch of $N_2$ and again it is clear that the perturbation is small but sufficient to require correction if accurate transition frequencies are to be deduced from measurements at energies in excess of a few mJ. It may be noted that the direction and magnitude of the shift provide access to the sign as well as the magnitude of $da/dR$. 


Fig. 2.
Optical Stark effect on SRS Q-branch of N₂ cooled in a free jet.

An excellent survey of the use of CARS and SRS for high resolution molecular spectroscopy is given in Ref. 1 and a compilation of molecules studied up until 1987 is given in Ref. 2. Most of the work has centered on improved frequency or linewidth measurements for small stable molecules but extension to larger and more reactive molecules is likely. As one example, Brown et al. [4] have recently applied pure rotational SRS to the study of the dicyanoacetylene molecule C₄N₂. The rotational constants and bond lengths of this linear molecule were not previously available, perhaps due to its lack of a dipole moment and its tendency to photopolymerize. Part of the interest in the properties of the molecule stem from its postulated existence in the atmosphere of Titan and probably in interstellar space. Fig. 3 shows the SRS spectrum of this molecule, obtained at 50 Torr. Each spectral "line" is actually a composite of the many hot band transitions that result because the molecule has low frequency bending modes at 107 and 263 cm⁻¹. Analysis gave an average B value of 0.04487(2) cm⁻¹ and an estimate of Bo of 0.0445(1) cm⁻¹, in good accord with a structure deduced in an accompanying electron diffraction measurement [4].

Fig. 3.
Pure rotational SRS spectrum of C₄N₂.
The short duration of the coherent Raman measurement with pulsed lasers has made the technique useful in the study of transient species such as those generated by laser or flash discharges. As an example, Triggs has recently obtained the CARS spectrum of the IR-forbidden symmetric CH stretch of the planar CH₃ radical, formed by 266 nm photolysis of CH₃I (Fig. 4). Data obtained at 0.05 cm⁻¹ resolution yield a band origin of 3004.34 cm⁻¹ and an upper state rotational constant of B₁₀₀₀ = 9.49662 cm⁻¹.

In addition to gas phase studies, the high resolution capability of the Coherent Raman techniques permits accurate measurement of frequencies, linewidths, and site splittings of molecular crystals at low temperatures. Such data are of intrinsic interest and have also proven quite useful in the study of the formation, supercooling and phase changes in microclusters formed in free jet expansions. Several such applications will be presented in the last part of this lecture.

ACKNOWLEDGMENTS: NSF and AFOSR research support is appreciated.


