

CARS IN CHEMISTRY

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Abstract

The experimental techniques used in a routine CARS apparatus, intended particularly for high temperature low pressure inorganic systems, are discussed. Particular emphasis is put on the lower frequency and of the spectrum (0-400 cm^{-1} Raman shift) with its attendant experimental difficulties.

Introduction

Coherent Anti-Stokes Raman Spectroscopy is by now a well established technique, backed by a moderate fund of practical experience, and reasonably predictive theory. We would like to draw particular attention to the work on selection rules and polarization phenomena,¹ published by Hanna and Yuratch of Southampton. Our purpose is to consider some of the situations in which a chemist might wish to use CARS as an alternative to conventional Raman, and some of the practical problems and solutions to them, encountered in using particular commercially available apparatus for the CARS spectrometer in the Chemistry Department at Southampton University. As inorganic chemists we are interested in the low frequency Raman shift region, 0-1100 cm^{-1} , with particular emphasis on 0-400 cm^{-1} . This creates some problems not otherwise encountered.

CARS and Conventional Laser Raman

The particular problems that face conventional Raman, and for which CARS may offer a solution, are those of fluorescent or thermal background radiation, and low sensitivity. The wide collection aperture may also be a problem when the sample area has to be enclosed. Although fluorescence in condensed media usually appears on the Stokes (red-shifted) side of a pump beam, this is not true of the resonance fluorescence encountered in the vapour phase. Thus the mere fact of obtaining an anti Stokes Raman signal, is not in itself enough to give discrimination against vapour phase fluorescence. (This use of CARS has been demonstrated in liquids, with benzene deliberately contaminated by Rhodamine 6G, for example). However, the laser-like quality of the CARS signal beam does offer considerable scope for discrimination against spontaneous processes emitting light into the whole solid angle. In the case of continuous background (thermal radiation, detector dark current) very good discrimination is inherently obtained from the pulsed source, gating the signal current in a box-car detector.

Similar use has been made of a much faster, picosecond pulsed source in conventional Raman,³ in an effort to gate out laser induced fluorescence, but the lower sensitivity of that process would mean that the shot noise problem (when a photon appears only once in every few laser pulses) would arise much sooner.

The enhanced sensitivity of CARS is however subject to one caveat. The number density of the medium is normally a square term in CARS, whereas spontaneous Raman is linear to this factor. Provided that the molecules do not photolyse, this may be countered by amplifying the pulsed CARS pump beam,

giving a favourable square law increase. The concentration of solute in a sufficiently dilute solution can become a linear factor again for CARS.² In this case the power limit for the pump beam is likely to be the onset of stimulated Raman or Brillouin scattering in the solvent.

Practical Sensitivity Limits

We will try and put some instructive numerical values to these ideas.

Most of our preliminary work was done on the CN stretching vibration of acetonitrile, since it appears in a particularly accessible region of the spectrum for us. We use a 15 n.sec. pulse from a Q-switched Nd/YAG laser, frequency doubled to 532 nm as the pump. For pure liquid acetonitrile, this had to be limited to about 50 kw peak power to avoid the generation of stimulated Raman. We have about 5 kw peak available in the probe, a flashlamp pumped dye laser. This can drop to 1 kw at the end of the dye range, with stale, or with less satisfactory dyes.

Under these conditions we detected about 10^6 photons per pulse. This was estimated by putting about 10^7 times attenuation in the signal beam, and observing that a photon pulse appeared only once in every few laser shots. This is an overall figure and could certainly be improved. Theory suggests a maximum of $\sim 10^8$ photons per pulse for these conditions.

We will assume that one photon in every few pulses represents a practical limit to detectivity, although this too might be improved with more efficient optical filtering and digital averaging. Pure liquid acetonitrile is some 20 Molar, so we could expect to achieve spectra at concentrations of about

$20 / 10^{3.5} \text{ M} \approx 0.01 \text{ M}$ using the powers described. This is completely realistic for a vapour, but in solutions the solute signal might be masked by the continuous or non-resonant background from the solvent. In our particular apparatus at the present time, we can achieve four times the pump power, taking us down to a normal limit of a few torr of vapour pressure. There is no great technical difficulty in achieving five times greater power at 532 nm, with an unstable resonator and/or amplifier, and we also intend to amplify the dye laser by up to four times, giving two orders of magnitude improvement in sensitivity overall. At some stage optical filtering and non-resonant background from lenses, other optical elements and air will certainly become limiting factors. Before leaving this subject we should point out that methane and hydrogen, for which detectivity limits are often quoted, are particularly favourable subjects for CARS because of their very narrow linewidths and high vibrational frequencies (which facilitate filtering of the signal).

Experimental Techniques

The building blocks of a CARS spectrometer are well known by now, and may be conveniently summarised as: 1) fixed frequency pump laser or source, 2) tunable probe laser, 3) beam combining element, 4) optical filter system, 5) detector, 6) signal processing electronics.

Lasers

Our system uses a Q-switched Nd/YAG laser (JK Lasers) as the initial pump source, with infrared peak power in the range of 1 megawatt upwards, and a Chromatix CMX4 flashlamp pumped dye laser as the tunable probe. This basic equipment was chosen for its proven reliability, ease of operation, even at narrow ($\sim 0.1 \text{ cm}^{-1}$) linewidth, and suitability of available power levels to

operation with vapours. Ideally we would like to be able to study vapours at fractions of a torr pressure, and the necessary additional power would be readily available with amplifiers added to the existing sources. Our set-up is not unlike that at N.R.L.^{2,4} except for their use of part of the Nd/YAG output, doubled or trebled, to pump a tunable dye laser.

Modification of source to cover the required spectral range

The spectral region covered by any CARS apparatus is the possible frequency difference between the pump and the probe. Good chemical practice requires the whole of the vibrational frequency range to be covered - say 0-4000 cm^{-1} - although as inorganic chemists we are most interested in the low end, about 0-400 cm^{-1} . The frequency range most easily covered by our equipment is 2000-3000 cm^{-1} , with the TEM₀₀ Nd/YAG output at 1.064 μ doubled to 532 nm, in conjunction with the best available dye, Rhodamine 6G, in the Chromatix. There are various ways of extending this range downwards. The most attractive is to down shift the 532 nm pump beam in some way, either by using it to generate stimulated Raman in a suitable medium, or by pumping a fixed frequency dye laser with it. This approach allows us to continue using Rhodamine 6G in the tunable dye laser, which is a great convenience. Apart from the price and performance of this dye, it can also be used in a 532 nm pumped amplifier.

Although we have generated stimulated Raman in liquid nitrogen and used it to run spectra, this is not the method of choice. The shifted output beam tends to wander, making overlap variable, and the conversion efficiency, although high, varies substantially from shot to shot, giving 20-30% intensity fluctuations - much worse than the incident 532 nm. The vibrational lifetime for liquid nitrogen is exceptional - several seconds⁵ - and it is possible that stirring or flowing would help.

Liquid nitrogen is the only medium we have discovered which reliably fails to generate stimulated Brillouin simultaneously with, or even instead of, stimulated Raman. The shifted radiation is also of as narrow linewidth as the incident, down to an estimated 0.06 cm^{-1} . With these advantages, it is unlikely that a more satisfactory medium could be found, unless high pressure Deuterium can be used at higher powers. The latter requires the use of extended red dyes, Sulphorhodamine, Cresyl Violet and Nile Blue, rather than Rhodamine 6G, but these are all moderately acceptable.

In view of the deficiencies of stimulated Raman, we propose to build a 532 nm pumped, manually tunable dye laser of appropriate linewidth for use as a CARS pump. Although the likely efficiency of such a device is only 10%, the Nd laser may be run multimode, producing greater power than in the TEM₀₀ mode required for direct use as a CARS pump. Should highly satisfactory green dyes become available for use in the Chromatix for low frequency work, it is still useful to be able to alter the resonance interactions with coloured samples.

Our best quality low frequency spectra to date have been run using green lasing dyes, Coumarin 504 and Fluorol 7GA, in the Chromatix. Our experience with Fluorol 7GA, for example, is that we can do a day's spectroscopy with a single charge, before the dye degrades and stops lasing. It is also soluble in water and detergent, which helps the mode structure and stability of the Chromatix enormously. This is because water has much better thermal properties than any organic solvent.

Pre-sample Optical Filtration

The attainable sensitivity for the CARS technique is highly dependent on

the efficiency with which spurious background can be eliminated. This remark applies to any spectroscopic method, but in the limit, where we have assumed a signal photon every few shots, it is clearly necessary to know with some confidence that a photon, when it does appear, is a genuine CARS photon. One source of considerable background intensity is flashlamp light and dye fluorescence emitted at the CARS signal frequency by the lasers. For small shifts, this problem is made much worse by partially collimated superradiance from the dye.

For work at large shifts, coloured glass filters are perfectly adequate. The Nd/YAG output may in any case be filtered free of visible radiation before frequency doubling. The dye laser must be filtered with an interference ('spike') filter or comparable device, and it is unlikely that this can be done with less than 50% loss. This is also true of a possible unscanned dye laser used to downshift the 532 nm.

For scans of greater than $10\text{--}20\text{ cm}^{-1}$ (or more, depending on the filter bandwidth chosen) the filter for the tunable laser must also be scanned. We propose to do this by angle tuning an interference filter to the appropriate function, or eventually by using a cam-scanned prism monochromator.

Beam combination

The pump and probe beams need to be collinear for vapours, so that combination must take place at the surface of a single element. Non-collinear phase matching in liquids is then easily achieved using the same element. A dichroic mirror is possible where the frequency separation is large (upwards of 1000 cm^{-1}), and we have used a krypton gas laser mirror with great success in the $2000\text{--}3000\text{ cm}^{-1}$ region ($532\text{ nm} + \text{Rhodamine 6G}$). At lower frequencies the requirements cannot be met with simple coatings, and although we have contemplated using spike filters or even a Fabry-Perot etalon, our present set-up uses a non-dichroic partial reflector. A simple calculation shows that a non-dichroic element should optimally combine $2/3$ of the pump beam with $1/3$ of the probe beam, and this arrangement may even be used to advantage in the regions of greater shift, with the remaining $1/3$ of the 532 nm pump used for a dye amplifier. As discussed in the next section, the path length difference must be kept very short to avoid synchronisation problems, and this deliberate rejection of part of the pump for an amplifier is of value only when the pump and probe powers are very different, as is the case with our equipment. Normally, residual $1.064\text{ }\mu$ would be doubled in a second crystal for this purpose. The green dyes used with a necessarily non-dichroic beam combiner cannot be pumped with 532 nm .

Various subterfuges may be used for beam combination, though most have some disadvantage. For example, we have tried combining our beams before generation of stimulated Raman in liquid nitrogen; our probe beam is well below the stimulated threshold, and this causes no problem. Unfortunately, however, non-resonant four wave mixing occurs in the liquid nitrogen, generating light at the CARS signal frequency which cannot easily be filtered out. We also propose to try combination in the infrared, before passing the $1.064\text{ }\mu$ through the doubling crystal, but the same objection will almost certainly apply.

In any scheme, the overlapped pathlength in air and optical elements must be kept small to avoid non-resonant background from these sources. We had a rather elegant scheme for reflecting the pump beam off the front mirror of the dye laser, but there was then nowhere that we could put a spike or other filter in the dye beam.

The initial alignment of the beams for correct spatial overlap always presents something of a problem. The Foucault knife edge test⁶ may be used. We have found that the longitudinal position of the beam waist can be judged accurately by eye-after which overlap at this point may be achieved by punching a hole in black PVC tape with one laser, and searching for the hole with the other at low intensity.

Synchronisation

The synchronisation of two different pulsed laser sources can present considerable problems on a nanosecond time scale. In our case we have to overlap the 15 nanosecond pulse of the Nd/YAG laser Q-switch, with the 2 microsecond emission from the dye laser. Even here the spark gap jitter of the dye laser makes difficulties, solved in our case by allowing dye laser flashlamp light, collected by a PIN diode, to trigger the Q switch Krytron. One spark gap can be allowed in a system, provided that it is allowed to set the fine timing. Our boxcar detector is triggered by the same method. Closer examination of the Q switched pulse shows that it is in reality a partial pulse train with a period of 2-3 nsec. and even narrower halfwidth. This does not matter until we use 'spare' 532 nm radiation from a second doubling crystal, to pump a dye amplifier. Then the pathlength difference must preferably be kept below a few cm., or possibly made equal to a little under a metre.

Optical filtration of the signal

This part of the system presents one of the most severe technical problems. There are some 2.5×10^{15} photons/millijoule for visible light, and with a few millijoules of 532 nm pump radiation, we require a discrimination of at least 10^{16} . We hardly expect to be able to use our kind of equipment at less than 50-100 cm^{-1} shift, and the good collimation of the beams must be a help, but it is clearly difficult to achieve this kind of discrimination without substantial loss of signal.

We have so far used a very simple, single prism premonochromator, followed by the double monochromator from an old Cary 81 Raman spectrometer. We have no hard figures for the throughput or discrimination of this arrangement, but it possibly transmits 10% of the signal, and it permits us to see signals of a few (collected) photons per pulse. We intend to continue using a prism, as the only suitable element to receive the whole of the initial power. At present we do not scan this, and therefore use it with rather wide bandpass. This limitation will have to be overcome in some way, but a simple linear scan may well cover an adequate range. Alternatively a very wide bandpass followed by an angle tuned interference filter may give us the extra rejection we still need. There is also a suggestion by Porto et al⁷ to use a Michelson interferometer as a spike rejection filter.

Detection and Signal Processing

We detect our signal on a modern, high gain wide range phototube, with moderate speed and timing jitter (EMI 9658A). With this tube we can collect all the signal from our original 15 nsec. pulse in a 100 ns gate width on our boxcar detector. The boxcar (Brookdeal 9415 + 9425) also integrates over the necessary number of shots with a 'sample and hold' circuit.

Ratioing

The only theoretically satisfactory way to ratio out laser fluctuations in

a non-linear experiment, is to generate a non-resonant reference signal. This could be done, for example, with high pressure argon. It is possible that some limited ranges could also be covered by materials with no broad, or very few, Raman active fundamentals (e.g. alkali halides, water or thoria).

Simple ratioing against dye laser output can be useful at the edge of a dye range, where output is varying rapidly with wavelength. This flattens the sensitivity curve, but cannot markedly improve signal to noise, unless the correct 15 nsec. of the pulse is selected.

We intend to assemble a referencing system in due course, probably using an optical delay in conjunction with the same post-sample filtering. This would be an obvious use for the radiation rejected by a non-dichroic beam combiner.

Background suppression

A number of schemes⁸ have been suggested for eliminating the non-resonant background which always accompanies the CARS resonances. The magnitude of this background is such that problems arise within the sample only when attempting to detect one species in the presence of an excess of another. Externally generated non-resonant background, from air and from optical elements, may trouble us more, and we may have to have recourse to one or other of the suppression techniques should this be the case.

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