

New exploratory experiments for Raman laser spectroscopy

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Introduction

The analysis of high-resolution rovibrational spectra is relevant because it allows the study of the structure and dynamics of molecules and molecular association, and how this changes under vibrational excitation. Topics in this context are the determination of equilibrium geometries of isolated molecules and of complexes, the study of the coupling of vibrations, intramolecular vibrational energy redistribution (IVR), tunnelling and rearrangement processes (for a recent overview, see ref.^[1]). Raman spectroscopy is an important technique in these studies, because it can provide complimentary information which is not available by IR spectroscopy due to different selection rules and experimental difficulties experienced accessing low-lying vibrational states. As an example, the symmetric CH- or OH-stretching vibrations of highly symmetric molecules like methane, cyclo-propane or cyclic formic acid dimer contain valuable information about coupling of vibrations, IVR processes and proton transfer reactions; these vibrations, however, are not IR active and can only be probed by Raman spectroscopy. Raman spectroscopic data is thus needed to complement information gathered from IR spectroscopy. Unfortunately, conventional Raman experiments suffer from low sensitivity and spectral resolution. Special, more advanced experimental techniques are therefore required to record Raman spectra with high sensitivity and sufficient spectral resolution.

Very promising high-resolution techniques are based on stimulating Raman schemes, the most prominent ones probably being inverse Raman spectroscopy and coherent anti-Stokes Raman spectroscopy (CARS). In Sheffield, we recently set up a stimulated Raman photoacoustic spectrometer using a Loan Pool laser system (NSL4, loans LP11C1/06 and LP19C2/06) which combines the sensitive detection of photoacoustic spectroscopy with coherent Raman scattering (photoacoustic Raman spectroscopy, PARS^[2]). Since the resolution is only limited by the bandwidth of the seeding dye laser (ca. 0.05 cm^{-1}), the scheme has much higher resolution than conventional Raman experiments employing a monochromator. Stimulated Raman experiments with photoacoustic signal detection allow measuring Raman spectra of gaseous species with high sensitivity and high spectral resolution. PARS has some similarities with CARS (besides the acronym); it shares its high resolution and has comparable sensitivity, but PARS has a much simpler set-up. PARS is also unique as it allows the observation of low frequency vibrational modes and pure rotational spectra without the need to separate the pump light and the seeding light/Raman signal.

In this article, we will introduce the Raman spectrometer, discuss calibration procedures and spectral resolving power, and show how this technique can be extended to the measurement of corrosive gases and hostile environments

using a modification of the optophone detection^[3,4] introduced by Zare and coworkers. We will also introduce a first application, the study of the anharmonic and Coriolis resonance system of cyclo-propane (C_3H_6) in the CH-stretching region near 3000 cm^{-1} ^[5] and present first tentative assignments.^[6]

Discussion

To set-up a stimulated laser Raman experiment, a strong Raman pump source at fixed wavelength and a tuneable stimulating Raman source are required. For this purpose, we modified a Nd:YAG pumped dye laser system (Continuum Sirah PrecisionScan, NSL4 on loan from the Laser for Science Facility, Rutherford Appleton Laboratory): After removing the main amplifier cell of the dye laser, the 532 nm light (second harmonic output of a diode seeded Nd:YAG laser, 10 Hz repetition rate) designated to pump the amplifier is guided around the dye

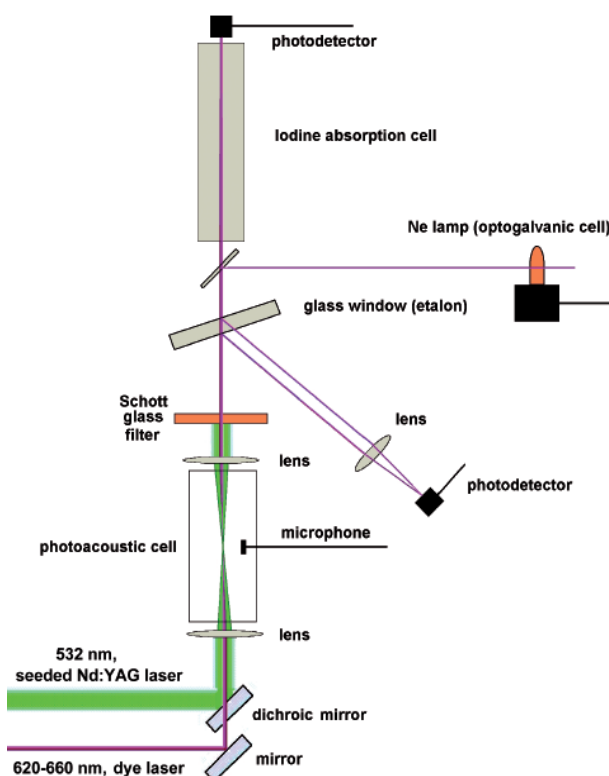


Figure 1. Key components of the photoacoustic stimulated Raman spectrometer, including focussing lens, photoacoustic cell with microphone, Ne-lamp for optogalvanic wavelength calibration, glass window as etalon, and iodine cell, with heating tape. The 532 nm green light is derived from the seeded Nd:YAG laser and serves as Raman pump, the red light in the 620-660 nm region is the stimulating Raman beam, derived from the dye laser system.

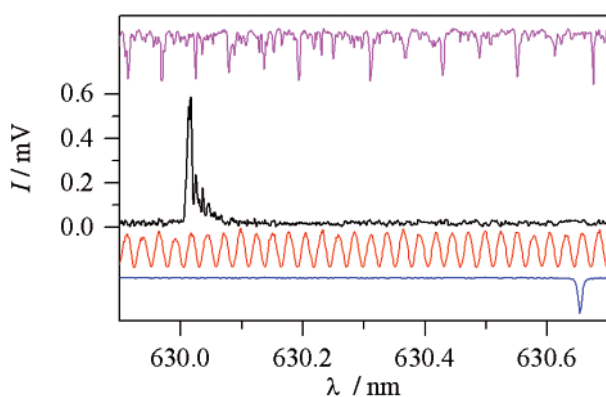


Figure 2. Typical scan, showing photoacoustic Raman spectroscopy (PARS) of 55 Torr methane CH_4 (trace in the middle) together with additional channels recorded simultaneously for wavelength calibration, iodine vapour absorption (upper trace), etalon fringes from a glass window and optogalvanic spectroscopy of Ne (lower traces).

laser cabinet and is attenuated to *ca.* 10 mJ/pulse. It serves as the Raman pump. The tuneable output of the dye laser in the 620–660 nm region (DCM dye, oscillator and preamplifier configuration, *ca.* 5 mJ/pulse, 0.05 cm^{-1} bandwidth according to the manufacturer's specifications) constitutes the stimulating Raman beam. Using a fast photo diode, we measured the temporal beam profiles. The green laser has a full width at half maximum (FWHM) of *ca.* 8 ns, and the dye laser a FWHM of *ca.* 4 ns. Both beams overlap perfectly in time (even without setting up a delay line), which is essential for the stimulation to be effective. Employing a dichroic mirror, the beams are combined and focused with a 10 cm focal length lens into a photoacoustic cell filled with 50–200 Torr vapour of a compound to be measured. If the energy difference between the laser photons corresponds to an allowed transition, molecules are promoted to a vibrationally excited state by the stimulated Raman process. By collisions, the vibrational excitation is subsequently converted into local heating. This creates a pressure wave which is picked up by a microphone (photoacoustic spectroscopy). The indirect detection of optical excitation is extremely sensitive. Tests have established that the photoacoustic signal is linearly dependent on both the stimulating Raman and the Raman pump power at our power levels (typically 5 mJ/pulse for the stimulation, 10 mJ/pulse for the pump). Higher Raman pump power would have been available, but excessive power causes decomposition of the sample vapour and soot formation on the windows of the photoacoustic cell.

Initial spectroscopic measurements showed that during a wavelength scan of the dye laser, a periodic deviation of the true wavelength from the wavelength reading of *ca.* $\pm 0.02 \text{ nm}$ exists. This is presumably due to imperfections of the sine drive of the grating within the dye laser oscillator, but this is totally unacceptable for high-resolution spectroscopy. Wavelength calibration is thus a great concern, since experimentally observed transitions should be reported with the highest possible accuracy. A system enabling accurate wavelength calibration of the tuneable dye laser was thus set-up and characterised, encompassing monitoring etalon fringes from the front and back reflection off a 5 mm thick glass window and

optogalvanic spectroscopy on Ne (using a conventional Ne glow lamp). The experimental set up is shown schematically in fig. 1. Three optogalvanic Ne lines are required to calibrate the etalon fringes (including the dispersion of glass). Observation of additional Ne lines then serves to assess and to verify the accuracy of the calibration, estimated as 0.03 cm^{-1} within a 20 nm scan range. More details on this inexpensive, but very effective calibration scheme can be found in ref. [7]. In addition, we checked our calibration by observing absorption lines of a reference absorption cell filled with iodine vapour, [8] kept at a temperature of *ca.* 80°C with heating tape to have an appropriate, elevated vapour pressure. During a typical wavelength scan, we thus record the photoacoustic Raman PARS signals simultaneously with etalon fringes, optogalvanic Ne lines and iodine absorption lines for accurate wavelength calibration of the dye laser (see fig. 2).

To characterise the potential of the set-up more fully, the ν_1 vibrational fundamental Raman transition (symmetric CH-stretching mode) of 55 Torr methane $^{12}\text{CH}_4$ has been observed. Fundamental IR and Raman transitions of methane have been studied in great detail before, in particular by a group of experimental and theoretical molecular spectroscopists in Dijon, France. [9] Methane is a small molecule, so its vibrational and rotational states are still tractable by theory, but yet it exhibits a very complicated rovibrational spectrum of transitions. Methane has thus become a test case for the interplay of theory with experiment in spectroscopy. Figure 3 shows the Q -branch of this ν_1 transition observed by PARS, together with a simulation using molecular parameters from ref. [9]. There is a very good agreement between experiment and

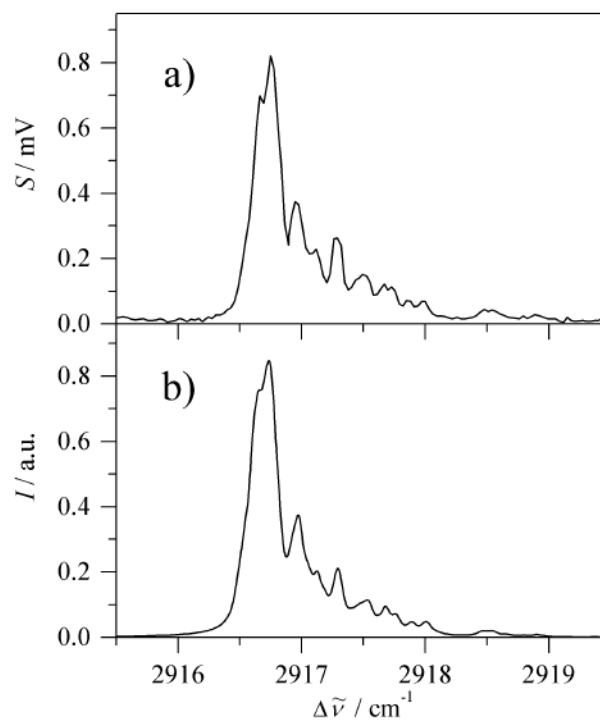


Figure 3. a) Stimulated photoacoustic Raman spectroscopy (PARS) of 55 Torr methane in a glass cell. b) Simulation of the ν_1 (A_1) fundamental Raman transition of $^{12}\text{CH}_4$ using previously published molecular parameters from ref. [9]; the stick spectrum has been convoluted with Lorentzian line shapes assuming an effective resolution of 0.08 cm^{-1} .

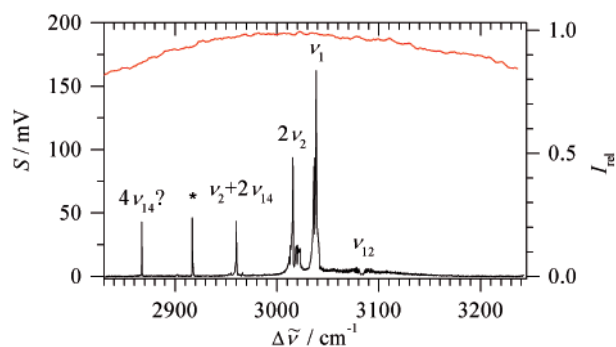


Figure 4. Stimulated Raman photoacoustic spectroscopy of some fundamental and overtone bands of cyclo-propane (C_3H_6 , 72 Torr). For *in situ* calibration, the sample also contained 6 Torr CH_4 (transition marked with asterisk, as in figure 3). The ordinate scale on the right and the upper curve refer to the relative dye laser (stimulating Raman) power during the scan.

theory, no intensity distortions are apparent, and there is a near perfect agreement between observed and calculated line positions, corroborating our calibration procedures. After convolution of the calculated stick spectrum with Lorentzian line shapes of FWHM 0.08 cm^{-1} , the experimentally observed line shapes are well reproduced, indicating that the effective experimental resolution is of the same order of magnitude. This finding is entirely compatible with the stated bandwidth of the dye laser, 0.05 cm^{-1} , and Doppler and pressure broadening of the order of 0.01 cm^{-1} , respectively (the bandwidth of the Nd:YAG laser as 532 nm Raman pump is negligible, since the Nd:YAG laser is seeded by a single-mode laser diode).

As a first scientific application of the spectrometer, high-resolution Raman spectra of gaseous cyclo-propane (C_3H_6) have been recorded in the region around 3000 cm^{-1} , encompassing many fundamentals and overtone transitions (see fig. 4, together with some assignments). This CH-stretching region is quite complicated due to the presence of many interacting vibrations,^[5] and has not been analysed in full detail yet. We have been able to measure partially rotationally resolved spectra of good quality which can be analysed to obtain improved molecular parameters and vibrational coupling constants which will indicate the flow of vibrational energy during IVR. As an example, we have observed for the first time a vibrational Raman band near 2870 cm^{-1} which we tentatively assign as $4\nu_{14}$. This observation is relevant, since $4\nu_{14}$ takes part in a Fermi anharmonic resonance system involving the $2\nu_2$, $\nu_2+2\nu_{14}$ and $4\nu_{14}$ vibrational bands. This resonance system is in turn connected to the ν_1 vibration by a Fermi anharmonic resonance between ν_1 and $2\nu_2$. As a next step, we want to model the entire band system of cyclo-propane in the $2800\text{--}3200\text{ cm}^{-1}$ region (vibrational analysis) which will yield insight into the coupling of vibrations and the transfer of energy between vibrations (IVR) in a small, prototype molecule.

Although the above mentioned work on Raman photoacoustic spectroscopy was highly successful, it showed one major limitation of photoacoustic spectroscopy: the microphones used to pick up the sound are exposed to the gases under investigation and they will suffer from corrosive, chemically reactive gases. An indirect

detection scheme avoiding direct exposure would thus greatly increase the use and applications of photoacoustic spectroscopy. As an example, one of our research interests is the observation of formic acid dimer in the gas phase; a preliminary experiment with the microphone configuration was not successful, because the microphone was destroyed within some minutes by the acid vapour. In order to circumvent this problem, we explored possibilities to detect acoustic waves inside the cell from outside, thus avoiding exposure of delicate equipment to corrosive gases. Based on some ideas reported previously in the literature,^[3,4] we fitted an etalon as acoustic sensor inside the detection cell, consisting of a pellicle beam splitter at a distance of *ca.* 2 mm to a glass surface (glass wedge). The pellicle is like a drum skin; acoustic waves distort its surface. In one configuration, an external green laser pointer shines from outside on the surface, and its deflection is monitored outside on a split photodiode. The acoustic distortion is monitored by deviations of the laser deflection. In another configuration, the interference pattern (fringe system) formed by back reflection of an external laser pointer off the pellicle and the glass surface is observed outside by a photodiode. Acoustic waves acting on the pellicle periodically change its distance to the glass surface, thus changing the interference pattern. Both configurations are suitable for remote detection of the acoustic wave generated by the stimulated Raman effect with good sensitivity. Comparison of Raman spectra of the ν_1 fundamental of methane recorded with a microphone, the light pointer and the etalon configuration show no intensity distortions and have comparable sensitivities, indicating a successful proof-of-principle. It is clear, however, that the material of the pellicle (nitrocellulose) will not sustain corrosive gases. In order to make it chemically more inert and resistant, we coated its surfaces with a thin layer of gold using a sputter coating apparatus for scanning electron microscopy; first tests have shown that it is indeed possible to obtain photoacoustic spectra with remote detection with this set up. In the future, we want to apply this detection technique to the formic acid dimer spectroscopy in the gas phase.

Conclusions

We have introduced the set-up of a high-sensitivity, high-resolution stimulated Raman spectrometer which is the first of its kind in the UK to our knowledge. We have discussed very effective and highly accurate calibration procedures and determined the spectral resolving power of the spectrometer. As a first application example, Raman spectra of the interacting vibrational states of cyclo-propane in the $2800\text{--}3200\text{ cm}^{-1}$ region have been recorded. Further analysis will reveal insight into the coupling of vibrations and the transfer of vibrational energy (IVR) in this small, prototype molecule. Finally we have discussed possibilities to extend the technique to the measurement of corrosive gases and hostile environments using remote detection of photoacoustic waves distorting a gold-coated membrane, either by a laser light pointer or by observing etalon fringes. In conclusion, we have shown that stimulated Raman photoacoustic spectroscopy (PARS) is a powerful and very promising tool for Raman spectroscopy of gas-phase molecules, since it combines very high sensitivity with high spectral resolving power. The scheme introduced is ideally suited to study the structure and dynamics of isolated molecules and molecular association by high-resolution Raman spectroscopy in the gas phase.

References

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