

STIMULATED RAMAN LASER EXCITATION OF SPONTANEOUS RESONANCE RAMAN SCATTERING

Richard P. VAN DUYNÉ and Keith D. PARKS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA

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The efficient conversion of the second and third harmonics of a Nd:YAG laser to near UV radiation in the 395–500 nm range by stimulated Stokes (and anti-Stokes) Raman scattering (SRS) in a 1 m Raman oscillator containing compressed H₂ or D₂ is used as an excitation source for spontaneous resonance Raman spectroscopy (RRS). SRS excited RR spectra are shown for the anion radical of tetracyanoquinodimethane (TCNQ).

1. Introduction

Spontaneous resonance Raman spectroscopy (RRS) is now widely recognized as a powerful tool for the study of the vibrational and electronic structure of molecules [1]. RRS is a fast, coherent light scattering process in which the energy of the incident photon derived from a laser source is selected to be close to or in coincidence with the energy of a vibronic transition in the target molecule. As a consequence of this resonance overlap condition, the intensity of inelastically scattered light is enhanced by factors of 10^3 – 10^6 compared to normal Raman scattering (NRS). This intensity enhancement endows RRS with the ability to study molecules: (1) ranging in size from diatomics to biological macromolecules [1, 2], (2) in any physical state or excited electronic state [1, 3], (3) in diverse environments such as electrochemical cells [3, 4], in vivo biological cells [4], and adsorbed on surfaces [5], and (4) under dynamic conditions over a wide range of time scales [1, 2, 6]. At the present time, the most severe limitation of RRS is that in practice it is not generally applicable to all molecules and all electronic transitions because of the limitations of conventional laser systems (viz., narrow or difficult achievable tuning range, low reliability*, expense, etc.).

* A case in point is the high-power cw krypton ion laser with laser wavelengths at 406.7, 413.1, and 415.4 nm. To date the reliability of these lasers has not been totally satisfactory.

In this letter we demonstrate an important step toward the achievement of broad-range tunability in a laser source applicable to RRS. We have shown that a broad-range, discretely tunable Raman laser [viz., stimulated Raman scattering (SRS) in H₂ or D₂ pumped by Nd:YAG harmonics] provides high S/N RR spectra, especially in the difficult accessible 360–460 nm region, when coupled with a multiplex Raman spectrograph detection system [2, 6]. To the authors' knowledge, this is the first application of a Raman laser to Raman spectroscopy. Broad-range, continuous tunability (viz., 200–2000 nm) will be implemented in the second stage of system development by using a Nd:YAG pumped dye laser as the pump source for SRS [7–10]. To demonstrate the potential of the stimulated Raman laser in RRS studies, we have obtained RR spectra for the anion radical of the strong electron acceptor species tetracyanoquinodimethane (TCNQ). TCNQ⁻ is a particularly acute example of the problems encountered in RRS studies when lasers with limited tunability are employed. The electronic absorption spectrum of TCNQ⁻ spans the range 200–950 nm in a series of bands (viz., ${}^2B_{3g} > {}^2B_{1u}^{(1)}$ 550–950 nm; overlapping ${}^2B_{3g} > {}^2B_{1u}^{(2)}$ and ${}^2B_{3g} > {}^2A_u$ 350–470 nm; and a more complex set of at least three transitions in the UV spanning 200–350 nm [3]). Consequently, the total RR information content extracted from TCNQ⁻ to date has been obtained from spectra excited with an Ar⁺ pumped cw dye laser in the 560–660 nm blue

tail of the lowest energy absorption band and a single RR spectrum excited with the 457.9 nm line of an Ar^+ laser in the red tail of the next higher energy absorption band [3, 11, 12]. Even though these spectra are acquired over a very limited subset of the possible excitation frequencies, they demonstrate great sensitivity to excitation wavelength. These RR data hint at the wealth of vibrational and electronic structure information yet to be revealed in TCNO^- as well as in a wide variety of other molecules if only they can be excited over a much broader wavelength range with a practical laser system. We believe that the Nd:YAG and/or Nd:YAG pumped dye laser pumped SRS laser will be the laser of choice in future RRS investigations.

2. Experimental

The experimental apparatus used for demonstrating SRS laser excitation of RRS is shown schematically in fig. 1. Second (532 nm) and third (355 nm) harmonic, linear polarized (horizontal), pulsed (10 Hz) beams were generated from the fundamental output (1.06 μm) of an unstable resonator, Q-switched

Nd:YAG laser (Quanta-Ray model DCR-1) using two, type II KD^*P non-linear crystals. A quartz Pellin-Broca prism (PBP) was used to select the desired Nd:YAG harmonic which was then focused into a 2.54 cm id \times 100 cm stainless steel high-pressure cell (HPC) by a 100 cm focal-length, plano-convex quartz lens (L1) positioned 25 cm in front of the entrance window to the HPC. The HPC is fitted with 1.27 cm thick \times 3.81 cm diameter plane quartz windows and is typically filled with H_2 or D_2 at a pressure of 480 kPa. This pressure was chosen as a compromise between higher pressures that optimize the conversion to high-order Stokes beams and lower pressures that optimize conversion to high-order anti-Stokes beams [8]. A 50 cm focal-length, plano-convex quartz lens (L2) located 25 cm behind the exit window of the HPC recollimates the output beam and reduces its diameter by a factor of 2 to ≈ 0.3 cm. The output beam consists of the partially depleted pump beam, several Stokes orders, and several anti-Stokes orders. A second quartz PBP was used to select the desired beam from the multiple frequency output beam generated in the HPC and direct it toward the sample area. Table 1 lists the Stokes and anti-Stokes wavelengths that can be generated in a

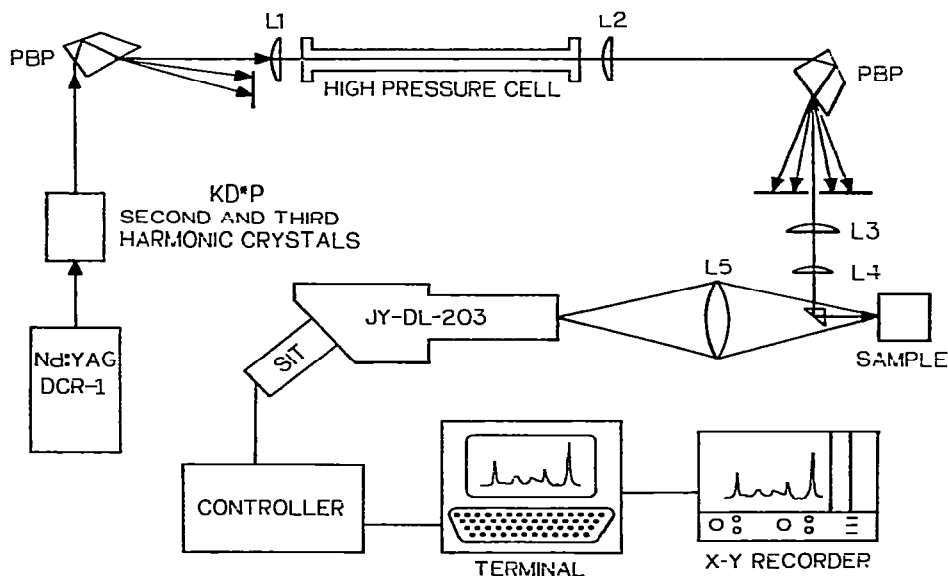


Fig. 1. Schematic diagram of the stimulated Raman laser and multiplex resonance Raman spectrograph.

Table 1
Excitation wavelengths available from a H₂ and D₂ Raman oscillator pumped by the harmonics of a Nd:YAG laser

SRS process AS _n , S _n	Nd:YAG harmonic $\pm n\omega_{\text{vib}}$ (μm)							
	1ω (1.064 μm)		2ω (0.532 μm)		3ω (0.355 μm)		4ω (0.266 μm)	
	H ₂ ^{a1}	D ₂ ^{b1}	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂
AS ₄	0.3843	0.4685	0.2823	0.3253	0.2231	0.2491	0.1845	0.2018
AS ₃	0.4574	0.5447	0.3199	0.3603	0.2459	0.2691	0.1998	0.2148
AS ₂	0.5647	0.6505	0.3689	0.4037	0.2739	0.2927	0.2178	0.2295
AS ₁	0.7378	0.8074	0.4357	0.4590	0.3091	0.3207	0.2395	0.2464
S ₁	1.907	1.560	0.6830	0.6325	0.4160	0.3967	0.2991	0.2890
S ₂	9.187	2.920	0.9536	0.7798	0.5029	0.4500	0.3415	0.3163
S ₃	—	—	1.579	1.017	0.6357	0.5199	0.3979	0.3492
S ₄	—	—	4.594	1.460	0.8639	0.6155	0.4768	0.3899

^{a1} $\omega_{\text{vib}} = 4155 \text{ cm}^{-1}$ for H₂. ^{b1} $\omega_{\text{vib}} = 2987 \text{ cm}^{-1}$ for D₂.

laser of this type. Under the focusing and gas pressure conditions cited above, $\approx 25\%$ of the pump energy (viz., 40–60 mJ pulse⁻¹ at 532 nm and 20–35 mJ pulse⁻¹ at 355 nm) was converted to each of the first two Stokes orders (S₁ and S₂); whereas, $\approx 10\%$ and 5% of the pump energy was converted to the first and second anti-Stokes orders (AS₁ and AS₂), respectively. The linewidths of the SRS output beams are not expected to exceed the linewidths of the pump beams [13, 14]. These are estimated to be $\approx 2 \text{ cm}^{-1}$ for the second harmonic and 1.5 cm^{-1} for the third harmonic.

Once generated and selected the SRS beam to be used for RR scattering experiments was line focused onto the sample cell by a combination of a 100 cm focal-length, plano-convex quartz lens (L3) and a 9 cm focal-length, cylindrical quartz lens (L4). L3 is required to compensate for the divergence of the SRS beam so that it does not spill over the 1.27 cm quartz 90° prism used to direct it to the sample. The spontaneous RR scattered light is collected using 180° backscattering geometry and a 7.5 cm focal-length, $f/1.1$ multi-element lens (Astro-Berlin, Tachonar) and imaged into the entrance slit of a triple holographic grating spectrograph (Jobin-Yvon model DL-203). The spectrograph is equipped with two concave holographic gratings (800 gratings mm⁻¹) mounted in subtractive dispersion to act as a scattered light rejection stage. Final dispersion of the RR light is accomplished with a plane holographic grating

(2400 gratings mm⁻¹). A 5.5 cm focal-length multi-element lens images the RR light onto the face of the multichannel detector. The detector size limited resolution of the system is 5–8 cm⁻¹ per channel depending on the excitation wavelength. The RR spectra reported here were detected with a 500 channel, uncooled silicon intensified target (SIT) vidicon tube (Princeton Applied Research Corporation (PARC) model 1254) which was controlled and read with the PARC model 1214 controller and model 1215 terminal. Hardcopy was generated from the analog output of the model 1215 and recorded on an XY plotter (Hewlett-Packard model 7004B). For comparison with the pulsed RR spectra generated by SRS excitation, cw RR spectra on the same samples were obtained at a nearly identical excitation frequency using the 457.9 nm line of an argon ion laser (Coherent Radiation Laboratories model CR-8). Preparation of TCNQ⁻ has been described previously [3, 4].

3. Results and discussion

The spontaneous RRS of TCNQ⁻ excited at 459.0 nm with the pulsed SRS laser (viz., 459.0 nm is the first anti-Stokes (AS₁) shifted line of the Nd:YAG second harmonic (2ω) in D₂; symbolized AS₁/ 2ω /D₂) and recorded with the multiplex Raman spectrographic detection system is shown in fig. 2.

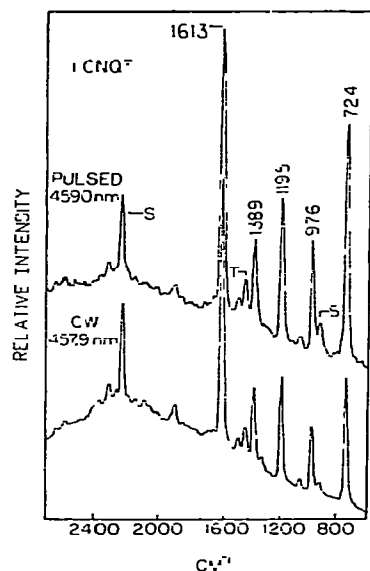


Fig. 2. Comparison of SRS pulsed (459.0 nm, 2.5 mJ pulse⁻¹, 600 pulses) and cw (457.9 nm, 25 mW, 60 s exposure) excited RR spectra of a 1×10^{-3} M solution of TCNQ⁻ in CH₃CN. S = CH₃CN solvent bands and T = 1453 cm⁻¹ band of TCNQ⁰.

Also shown in fig. 2 is the RRS of the same TCNQ⁻ sample excited at 457.9 nm with a cw Ar⁺ laser and recorded with the same detection apparatus. Comparison of these pulsed with cw RR spectra taken at nearly identical excitation wavelengths yields the following conclusions: (1) the SRS laser produces spontaneous RR spectra with excellent S/N, (2) all of the Raman lines observed in the cw spectrum are observed in the SRS excited spectrum, and (3) no new Raman lines are observed in the pulsed spectrum. The exact one-to-one correspondence of all the Raman frequencies and lineshapes demonstrate that no gross, irreversible damage was induced by the pulsed SRS laser even though its peak power density in the 4×10^{-3} rectangular beam area produced at the sample by L4 was 90 MW cm⁻². Further evidence against irreversible laser photodamage is that electronic absorption spectra taken before and after laser irradiation were identical. A relatively minor difference between the spectra in fig. 2 is the relative intensity pattern. The intensities of the 724, 976, and 1195 cm⁻¹ lines (relative to the intensity of the 2252 cm⁻¹ solvent (S) line which acts as an internal

standard) are 50–100% larger in the pulsed spectrum than in the cw spectrum. The relative intensities of the 1613, 1453 (T), and 1389 cm⁻¹ lines, on the other hand, are $\leq 30\%$ larger in the pulsed than in the cw spectrum. Possible causes of this intensity pattern are: (1) photoelectron ejection from TCNQ⁻ where electron recombination is delayed by intervening chemical reactions until termination of the laser pulse and (2) onset of stimulated Raman scattering (perhaps resonance enhanced) such as has been observed by Woodruff [6]. An analysis of the intensity behavior of the 1453 cm⁻¹ line of TCNQ⁰ (i.e., the electrolysis of TCNQ⁰ to form TCNQ⁻ was only $\approx 95\%$ complete so that there is some residual TCNQ⁰ even in the cw excited spectrum) and the 1389 cm⁻¹ line of TCNQ⁻ rules out the photoelectron ejection mechanism at these incident laser power densities. A more complete report of the intensity pattern in SRS excited RRS will be reported elsewhere [15].

Fig. 3 shows the RR spectrum of TCNQ⁻ excited at 416.0 nm with the S₁/3 ω /H₂ line of the SRS laser. This excitation wavelength is extremely close to the absorption maximum (viz., 420 nm) of the 350–470 nm band of TCNQ⁻ where one expects to observe maximum RR enhancement. The dramatic increase in the RR information content of this spectrum relative to the 459.0 nm excited spectrum is shown in fig. 3 by scaling both spectra so that the 931 cm⁻¹ solvent bands are equal in intensity. Not only are the intensities of 724, 976, 1195, 1389, and 1613 cm⁻¹ bands greatly enhanced in the 416.0 nm excited spectrum but, in addition, one observes many combination bands (C₁–C₇) and the first overtone (O) of the 1613 cm⁻¹ vibration. These data clearly illustrate the importance of developing broadly tunable laser sources for RRS so that maximum enhancement can be achieved and so that detailed excitation profiles which reveal the dependence of line intensity on excitation wavelength can be measured. A more complete study of SRS excited TCNQ⁻ RRS showing the excitation profiles obtained with the 396.7, 435.7, and 450.0 nm as well as the 416.0 and 459.0 nm lines will be published elsewhere [15].

In summary we predict that because of its simplicity, high average power, and broad tuning range, the SRS laser will have a significant impact on the future of RR spectroscopy. Furthermore, there are a large

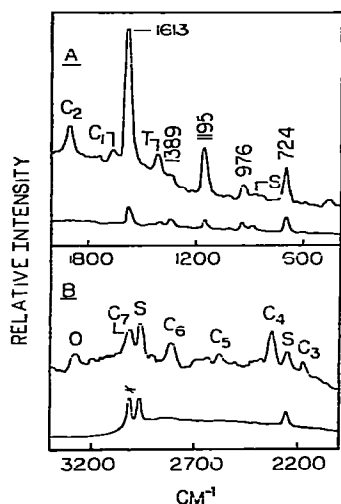


Fig. 3. (A) SRS laser excited resonance Raman spectra of 1×10^{-3} M TCNQ⁻ in CH₃CN from 400–2000 cm⁻¹. Upper spectrum; 416.0 nm, 1 mJ pulse⁻¹, 600 pulses. Lower spectrum; 459.0 nm, 2.5 mJ pulse⁻¹, 600 pulses. The intensities are scaled so that the 930 cm⁻¹ CH₃CN solvent band is equal in both the upper and lower spectrum. (B) Same as (A) except from 2000–3600 cm⁻¹. S = CH₃CN solvent bands; C = combination bands; O = overtone; * = laser line. C₁ = $\nu_6 + \nu_5$, C₂ = $\nu_5 + \nu_7$, C₃ = $\nu_5 + \nu_6$, C₄ = $\nu_3 + \nu_7$, C₆ = $\nu_3 + \nu_6$, C₆ = $\nu_3 + \nu_5$, C₇ = $\nu_3 + \nu_4$, and O = $2\nu_3$ where $\nu_3 = 1613$ cm⁻¹, $\nu_4 = 1389$ cm⁻¹, $\nu_5 = 1195$ cm⁻¹, $\nu_6 = 976$ cm⁻¹ and $\nu_7 = 724$ cm⁻¹.

number of options for improving the quality of the SRS laser over that represented by this preliminary study. Future publications from our laboratory will deal with: (1) extending the tunability of the SRS laser by using a high peak power dye laser, (2) using gas mixtures in the SRS cell to improve tunability, and (3) using waveguides [9] and/or Raman amplification stages to increase power and beam quality in the high order Stokes lines.

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