

Prolonged-excitation coherent Raman spectroscopy with spectral resolution beyond the transition linewidth using two tunable picosecond dye lasers

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A time-resolved coherent anti-Stokes Raman technique is demonstrated that yields a spectral resolution beyond the linewidth obtained in spontaneous Raman spectroscopy. Two picosecond dye lasers, independently tunable with low timing jitter, are used. The coherent material excitation is generated by long pump pulses and monitored by short delayed probing pulses. Transiently narrowed Raman spectra are recorded by scanning the lasers over the resonances of interest and simultaneously monitoring the coherent scattering signal as a function of the excitation frequency. The technique is applied to molecular vibrations in liquids. The differences between the technique presented and standard coherent anti-Stokes Raman spectroscopy are demonstrated.

INTRODUCTION

Single homogeneously broadened transitions show Lorentzian-shaped lines in stationary experiments. The spectral width $\Delta\omega$ is determined by the lifetime T of the levels, i.e., by energy relaxation in rarified gases or by phase relaxation in the condensed phase. The homogeneous width buries the spectroscopic information when several closely spaced transitions overlap. In this case, steady-state techniques, e.g., spontaneous Raman spectroscopy and standard coherent anti-Stokes Raman spectroscopy (CARS), display a broad and featureless band. It is promising to use line-narrowing methods that reduce the individual spectral bandwidths and, as a consequence, reveal details of the transition frequencies and intensities in congested regions.

In order to reduce the spectral width of homogeneously broadened transitions, the experimental observation time must be longer than the lifetime T . This situation may be achieved in a transient coherent experiment in which the specific experimental conditions determine the observation time.¹⁻⁸ Time-resolved spectroscopy can produce linewidths considerably narrower than homogeneously broadened lines of steady-state spectroscopy. Various transient line-narrowing experiments based on gated excitation or gated observation have been suggested to achieve subnatural spectra of single atomic transitions.¹⁻⁵ Recently, a different transient line-narrowing technique using time-resolved coherent Raman spectroscopy was developed: After a short excitation process the line narrowing results from prolonged interrogation of the molecular excitation.⁶ Coherent Raman scattering of a long Gaussian-shaped probe pulse was investigated. The observed lines have a Gaussian shape and are, for a long duration of the probe pulse, narrower than the stationary lines. This technique was successfully applied to molecular vibrations in liquids, in which it permitted narrowing of single lines⁶ and resolution of individual transitions in congested spectral regions.⁷

In this paper we present the first reported experimental application of an *alternative* line-narrowing technique well

suited for the study of molecular transitions in liquids.⁸ In this technique the line narrowing is performed in a prolonged (Raman) excitation process of the molecular vibrations followed by delayed probing of the coherent excitation. Recording the probing signal while tuning the excitation frequency gives the narrowed spectrum. A favorable light source proves to be a twin dye-laser system consisting of two synchronously mode-locked dye lasers that generate continuously tunable picosecond pulses. As an example, we present transiently narrowed spectra of pure pyridine and of pyridine-methanol mixtures.

THEORY

In quasi-stationary CARS, two light fields E_L and E_S of respective frequencies ω_L and ω_S and of long durations ($t_p \gg T$) are focused into the sample. The angle between the two beams has to be adjusted in order to obtain phase matching $k_A = 2k_L - k_S$ (Ref. 9) for efficient coherent anti-Stokes light production at $\omega_A = 2\omega_L - \omega_S$. In the plane-wave approximation with $\vec{E}_j(t) = E_j(t)\exp(-i\omega_j t + ik_j x) + \text{c.c.}$, we obtain for the anti-Stokes field E_A

$$\frac{\partial E_A}{\partial x} \propto E_L^2 E_S^* \chi^{(3)} = E_L^2 E_S^* (\chi_{\text{RES}}^{(3)} + \chi_{\text{NR}}^{(3)}), \quad (1)$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility responsible for the coherent anti-Stokes light. When the frequency difference $\omega_L - \omega_S$ is close to a molecular resonance, the linear susceptibility may be separated into a resonant part $\chi_{\text{RES}}^{(3)}$ that is due to a vibration at frequency ω_0 and a nonresonant term $\chi_{\text{NR}}^{(3)}$ resulting from distant (electronic) resonances. When $\chi_{\text{NR}}^{(3)}$ is negligible, the anti-Stokes spectrum $I_A(\omega) \propto |E_A(\omega)|^2$ peaks at $\omega_A = 2\omega_L - \omega_0$ and has the same width as the spontaneous Raman band. For a finite value of $\chi_{\text{NR}}^{(3)}$ a more complex spectrum results from the interference of the nonresonant and the resonant parts of $\chi^{(3)}$, giving asymmetric lines.⁹ The different time dependence of $\chi_{\text{NR}}^{(3)}$ and $\chi_{\text{RES}}^{(3)}$ may be used to reject the nonresonant contribution in

a transient experiment.¹⁰ We describe the resonant vibrational excitation by the time-dependent coherent amplitude q and use light pulses E_L and E_S for its excitation and a delayed pulse E_{L2} for the probing process. The anti-Stokes field E_{AS} generated by a phase-matched probing pulse is obtained by generalization of Eq. (1)¹⁰

$$\frac{\partial E_{AS}}{\partial x} \propto E_{L2}\bar{q}^* + \chi_{NR}^{(3)} E_L E_{L2} E_S^*. \quad (2)$$

The equation of motion of the coherent amplitude $\bar{q} = q \exp(-i\omega_0 t) + \text{c.c.}$ has the form

$$\frac{\partial^2 \bar{q}}{\partial t^2} + \frac{2}{T_2} \frac{\partial \bar{q}}{\partial t} + \omega_0 \bar{q} = \bar{A}(t), \quad (3)$$

where $\bar{A}(t) = A(t)\cos(\omega t) \propto E_L E_S^* \cos[(\omega_L - \omega_S)t]$ is the driving force and T_2 is the dephasing time of the molecular transition. One readily sees from expression (2) that the contribution of the nonresonant susceptibility vanishes when there is no overlap between the exciting and probing light fields, whereas the slow decay of the coherent amplitude q may still give a signal from the resonant excitation. Thus delayed probing removes the disturbing effects of $\chi_{NR}^{(3)}$ from the CARS spectrum.^{10,11}

Now we discuss the line-narrowing effect found by our technique. We measure the coherent anti-Stokes signal E_{AS} with a short probing pulse E_{L2} at a delay time t_D where the exciting force is negligible. The scattered anti-Stokes field is proportional to the coherent material excitation at the corresponding delay time, $E_{AS} \propto q(t_D)$. A general solution for q at the time t_D has the form

$$q(t_D, \Delta\omega) \propto \exp(-t_D/T_2) \int_{-\infty}^{t_D} dt' \exp(i\Delta\omega t') A(t') \exp(t'/T_2), \quad (4)$$

where $\Delta\omega = \omega_L - \omega_S - \omega_0$ indicates the frequency mismatch between the driving force at $\omega_L - \omega_S$ and the Raman resonance at ω_0 . When the driving force $A(t')$ has the duration t_p , the integrand vanishes for times $t_D \gg t_p$. We note that, for large times t_D , expression (4) represents the Fourier transform of the excitation pulse $A(t')$ times an exponentially rising function $\exp(t'/T_2)$. With a Gaussian-shaped excitation, i.e., when the two pulses at ω_L and ω_S have a Gaussian shape, the Fourier transform leads to a Gaussian frequency dependence of $q(\Delta\omega)$ and E_A , independent of the dephasing time T_2 .⁸ The frequency width of this Gaussian function is determined only by the duration t_p of the driving pulse. The observed coherent anti-Stokes spectrum is narrower than the Lorentzian-shaped homogeneous line when long excitation with pulse durations $t_p > 1.4 T_2$ is used. Consequently, measuring the coherent anti-Stokes signal at late delay times as a function of the frequency mismatch $\Delta\omega$, one observes a line shape that is narrower than the spontaneous-transition linewidth.

EXPERIMENT

Characteristics of the Twin Dye-Laser System

In the experiments we apply a dual picosecond dye-laser system consisting of two independently tunable dye lasers

synchronously pumped by a cw mode-locked Ar⁺-ion laser. The Ar⁺-ion laser produces laser pulses at a repetition rate of 75.77 MHz. The output power of 750 mW is split into two parts and serves to pump two dye lasers synchronously, one with Rhodamine 6G dye and one with DCM dye. The output of the two dye lasers amounts to approximately 35- and 45-mW average power at 600 and 640 nm, respectively. Two plates birefringent filters and output couplers with $T = 20\%$ were used. Figure 1(a) shows a semilogarithmic plot of the background-free autocorrelation trace of the dye laser at $\lambda = 640$ nm. The autocorrelation trace shows a peak-to-background ratio of 5×10^5 and is approximately sech^2 shaped. The FWHH is 4.9 psec, suggesting a pulse duration of 3.1 psec. Similar properties are found for the second laser at $\lambda = 600$ nm. Of interest is the cross-correlation function between the laser pulses at 600 and 640 nm, measured by background-free sum-frequency generation. In Fig. 1(b) we find a FWHH of 6.2 psec. The temporal jitter τ_j between the two laser pulses may be estimated from the widths of the cross-correlation function τ_{cc} and the durations τ_{600} and τ_{640} of the two laser pulses.¹³ One calculates that $\tau_j = (\tau_{cc}^2 - \tau_{640}^2 - \tau_{600}^2)^{1/2}/2 = 2.2$ psec. The accuracy of the temporal synchronization of the two lasers depends on several factors, including thermal and flow instabilities in the dye jet streams, variation of the pump power, acoustic and thermal fluctuations of the cavity lengths, and mechanical instabilities. The jitter was minimized in our twin dye-laser system by (1) mounting all mirrors on a rigid construction consisting of two solid Invar bars, (2) stabilizing the length of both dye lasers by a single Zerodur ceramic rod, and (3) adjusting the pump power and the cavity losses in such a way that the threshold and laser gain of both laser cavities have similar values. Thus both lasers follow variations in the pump power in a similar way and preserve temporal synchronization.

We also investigated the emission spectra of the laser pulses and found a bandwidth product of $\Delta\nu \times t_p = 0.46$ in both cases, which somewhat exceeds the theoretical value of $\Delta\nu \times t_p = 0.32$ for sech^2 -shaped pulses. This observation indicates the presence of a small chirp on the pulses. The bandwidth product could be improved by slightly shortening the cavity length of the dye lasers. At the same time, the jitter was reduced to 1.5 psec. But now shoulders appeared approximately 3 orders of magnitude below the peak of the autocorrelation and cross-correlation functions, suggesting weak secondary pulses.

To our knowledge, the smallest jitter between two dye lasers pumped by an Ar⁺ laser was reported to be 2.7 psec.¹² Recently, with a Nd:YAG-pumped dye-laser system, a jitter of 1.4 psec was reported.¹³ In Ref. 13 the correlation traces were presented on a linear plot, giving no information on structural details several orders of magnitude below the peak.

The important features of our laser system are the following: (1) ultrashort tunable sech^2 -shaped pulses are obtained with exceptionally clean autocorrelation curves and pulse durations down to 3 psec. (2) The temporal jitter between the laser pulses of the two dye lasers operating at different frequencies is low. The pulses are well suited for our high-resolution CARS for pump and probe experiments in which different wavelengths are required. (3) The tuning range of the difference frequency extends from zero to 3000 cm^{-1} when Rhodamine 6G and DCM are used as laser dyes.

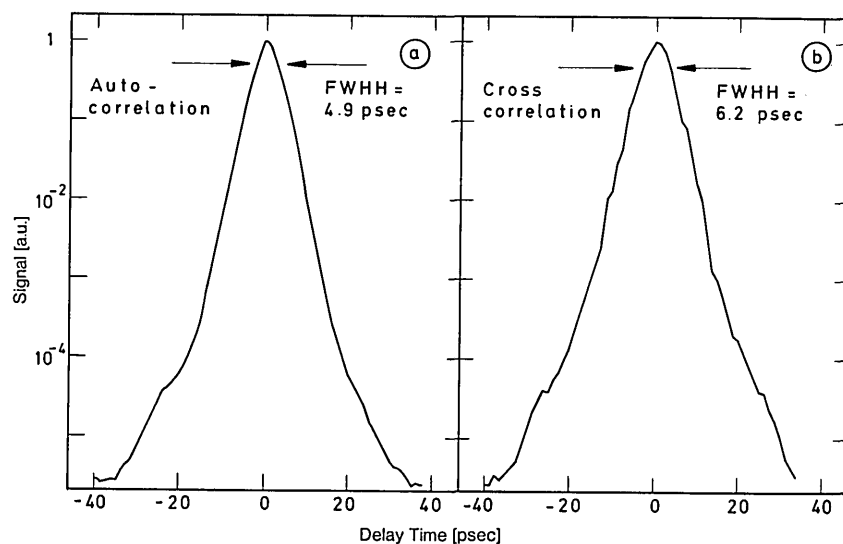


Fig. 1. (a) Semilogarithmic plot of the measured autocorrelation function of the DCM dye laser operated at 640 nm. The FWHH is 4.9 psec. (b) Cross correlation of the Rhodamine 6G laser and the DCM dye laser with FWHH 6.2 psec.

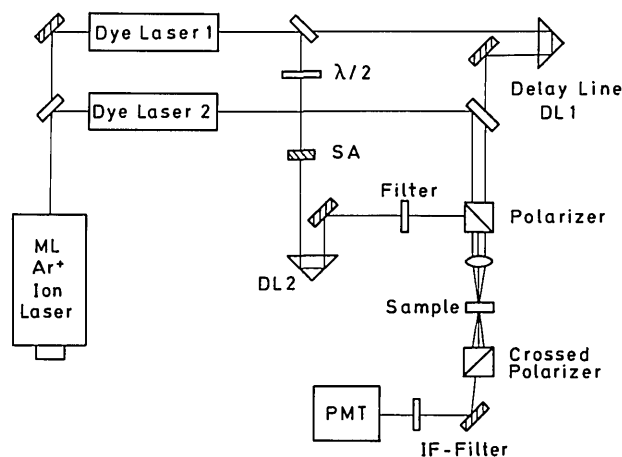


Fig. 2. Experimental setup for high-resolution Raman spectroscopy consisting of delay lines DL1 and DL2, polarizers, photomultiplier PMT, and dye jet as saturable absorber SA.

Experimental System

A schematic of the experimental setup used for the line-narrowing transient Raman spectroscopy is shown in Fig. 2. The pulses from the two dye lasers at frequencies ω_L and ω_S are horizontally polarized. They traverse the first polarizer and are focused into the sample. With the help of the optical delay line DL1 the pulse E_S is adjusted to coincide temporarily in the sample with pulse E_L . In the present experiment both lasers emit pulses with the same duration of $t_p \approx 12$ psec and spectral width of 1.0 cm^{-1} . Three plate birefringent filters in combination with glass étalons in the dye-laser cavities were used. The weak probing pulse E_{L2} is split off from the pumping field E_L by a beam splitter and shortened by approximately 50% in the saturable-absorber jet SA. Of special importance is the steep rise of the probe pulse that we generate in the nonlinear absorber. The probe pulse is properly positioned in time by the delay line DL2 and focused into the sample. The probing pulse has vertical polarization. The exciting and probing pulses cross in the sample at angles adjusted to obtain phase matching for coherent anti-Stokes generation. Anti-Stokes light of vertical polarization trans-

mitted by the second polarizer P and the bandpass interference filter IF is recorded by a cooled photomultiplier tube PMT and a phase-sensitive detection system. The interference filter has a bandwidth of 100 cm^{-1} , which covers the frequency range of the anti-Stokes emission. Our experimental system has a highly favorable dynamic range. The coherent anti-Stokes signal of the ν_1 mode (990 cm^{-1}) of pyridine could be measured as a function of the time delay of the probing pulse over 5 orders of magnitude.

RESULTS AND DISCUSSION

Two experiments are discussed here. The technique of prolonged excitation and delayed probing is applied first, to a single vibrational mode and second, to a congested frequency range of overlapping bands.

In Fig. 3 experimental results of the ν_1 ring mode¹⁴ of liquid pyridine at 990.7 cm^{-1} are presented. Three spectra are recorded by three different experimental techniques. (1) Figure 3(a) shows the spontaneous (polarized) Raman spectrum taken with a standard Raman system of 0.5-cm^{-1} spectral resolution. The band has a nearly Lorentzian shape and a width (FWHM) of 2.1 cm^{-1} . Considering the instrumental resolution, we obtain a spectral width of the ν_1 mode of pyridine of 1.9 cm^{-1} . (2) The CARS curve of Fig. 3(b) is recorded with the picosecond equipment as described but with zero time delay between the exciting and the probing pulses. This band is asymmetric, and the peak position does not coincide with the resonance frequency of the molecular mode. The interference of resonant and nonresonant susceptibilities $\chi^{(3)}$ leads to the shift of approximately 0.5 cm^{-1} . The CARS spectrum has a width of 3.1 cm^{-1} and is considerably broader than the spontaneous Raman line. (3) With a delayed probe pulse one obtains a completely different CARS band (right-hand side of Fig. 3). Now the band is narrower, with a width of $\Delta\nu_{\text{coh}} \approx 1.4 \text{ cm}^{-1}$, which is even narrower than the spontaneous Raman line with $\Delta\nu_{\text{spont}} \approx 2.1 \text{ cm}^{-1}$. The band is symmetric, and its peak is found precisely at the same frequency of 990.7 cm^{-1} as the spontaneous Raman spectrum. The prolonged excitation process and the delayed probing provide us with two impor-

tant features. They reject the contribution of the nonresonant susceptibility and they narrow the spectrum beyond the spontaneous Raman width.

We now proceed to the more complicated situation in which several overlapping transitions give rise to an unresolved broad spontaneous Raman band. As an example, we present data of mixtures of pyridine and methanol, for which different hydrogen-bonded species are expected. The hydrogen-bonded complexes between pyridine and methanol change the vibrational spectrum in the region of the ν_1 mode of pyridine.^{14,15} A new band appears around 998 cm^{-1} . Spontaneous Raman investigations have shown that this band is broad, slightly changing in shape and frequency position with concentration.¹⁶ In Fig. 4(a) the spontaneous Raman spectrum of a mixture of pyridine-methanol is depicted (0.5- M fraction of pyridine). The band on the left-hand side peaking at 990.5 cm^{-1} corresponds to free pyridine molecules discussed above (see Fig. 3). The broad band at the right-hand side of Fig. 4(a) at 998 cm^{-1} is due to hydrogen-bonded pyridine-methanol complexes.

A standard coherent anti-Stokes Raman spectrum without time delay ($t_D = 0$) between excitation and probing is depicted in Fig. 4(b) (dashed line). The broad spectrum in the hydrogen-bonded region gives no new information compared with the spontaneous spectrum of Fig. 4(a).

A drastically different Raman spectrum is obtained by the prolonged excitation and delayed probing technique presented in this paper. In Fig. 4(b), solid curve, we show a narrowed transient coherent anti-Stokes spectrum. The following points are of interest here: (1) The pyridine line around 990.5

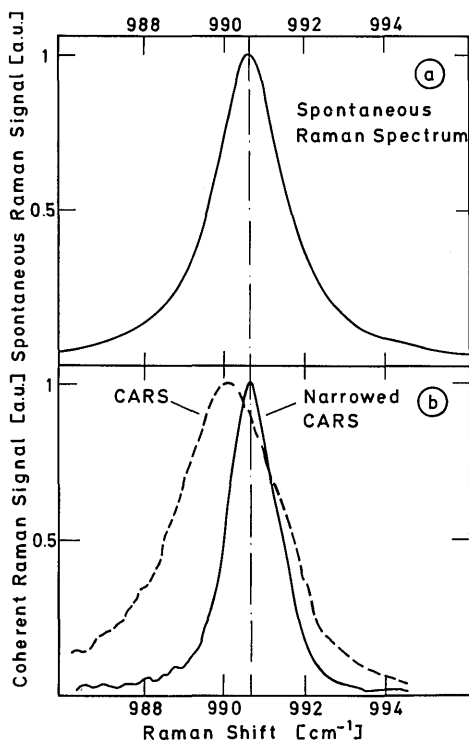


Fig. 3. (a) Spontaneous Raman spectrum of the ν_1 mode (990 cm^{-1}) of pyridine taken with a resolution of 0.5 cm^{-1} . (b) Comparison of CARS and narrowed CARS measurements of the same Raman line. Both spectra were taken with the setup of Fig. 2. In the narrowed CARS experiment the weak probe pulse was delayed with respect to the excitation pulses by approximately 20 psec.

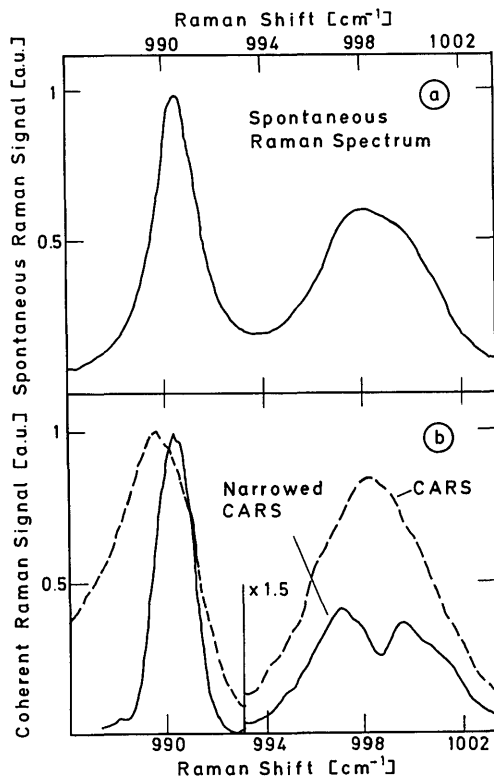


Fig. 4. (a) Spontaneous Raman spectrum of a mixture pyridine-methanol with 0.5- M concentration of pyridine taken with a Raman spectrometer with 0.5-cm^{-1} resolution. (b) Coherent anti-Stokes Raman spectrum of the same mixture taken at $t_D = 0$ (dashed curve) and $t_D = 15\text{ psec}$ (solid curve). Two peaks can be resolved under the broad band around 998-cm^{-1} in the delayed transient CARS experiment.

cm^{-1} is narrower than in the spontaneous spectrum. This result agrees with Fig. 3. (2) The pyridine band and the bands of the complexes are well separated. (3) Two distinct lines at 997 and 1000 cm^{-1} are clearly resolved in the spectral range, where the spontaneous Raman spectrum shows one broad and featureless band. (4) The position of the transiently narrowed lines does not vary with concentration. (5) The strength of the lines varies with concentration. This observation explains the changes in shape and position of the broad hydrogen-bonded band in the spontaneous Raman spectrum.

The data of Fig. 4(b) clearly demonstrate the existence of distinct hydrogen-bonded complexes of pyridine and methanol.

COMPARISON WITH OTHER LINE-NARROWING TECHNIQUES

We now compare the present line-narrowing technique that uses prolonged excitation and delayed probing with the recently introduced method of short excitation and prolonged interrogation (SEPI). Theoretically, the line-narrowing process is similar for both techniques.⁸ The prolonged excitation or the prolonged probing process is essentially for improved spectral resolution. The two techniques are essentially different on technical grounds: (1) In the SEPI technique the short (sometimes broadband) excitation process requires only stepwise-tunable laser pulses and one clean (bandwidth-limited) pulse for probing. Certainly, contin-

ously tunable pulses are advantageous.¹⁷ On the other hand, a high-resolution spectroscopic device is needed to resolve the (low-level) coherent Stokes or anti-Stokes spectra. (2) In the prolonged excitation technique a high-resolution spectroscopic device is not required. Spectral resolution is obtained by tuning one of the two exciting laser pulses. The second technique necessitates two bandwidth-limited light pulses of low time jitter for the prolonged excitation process. When such pulses are available, narrowed coherent Raman spectra may be recorded with ease similar to that in standard CARS.

CONCLUSION

A novel line-narrowing coherent Raman spectroscopy based on prolonged excitation and delayed probing of a vibrational transition is presented. The line-narrowing technique was realized experimentally by using a synchronously pumped mode-locked twin dye-laser system. The basic results are as follows: (1) The technique presented permits narrowed Raman spectra to be obtained. (2) Spectra of high resolution may be recorded without a spectrograph. (3) The nonresonant (electronic) susceptibilities do not disturb the observations. The observed signal peaks give the frequencies of the Raman transitions directly.

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