Title

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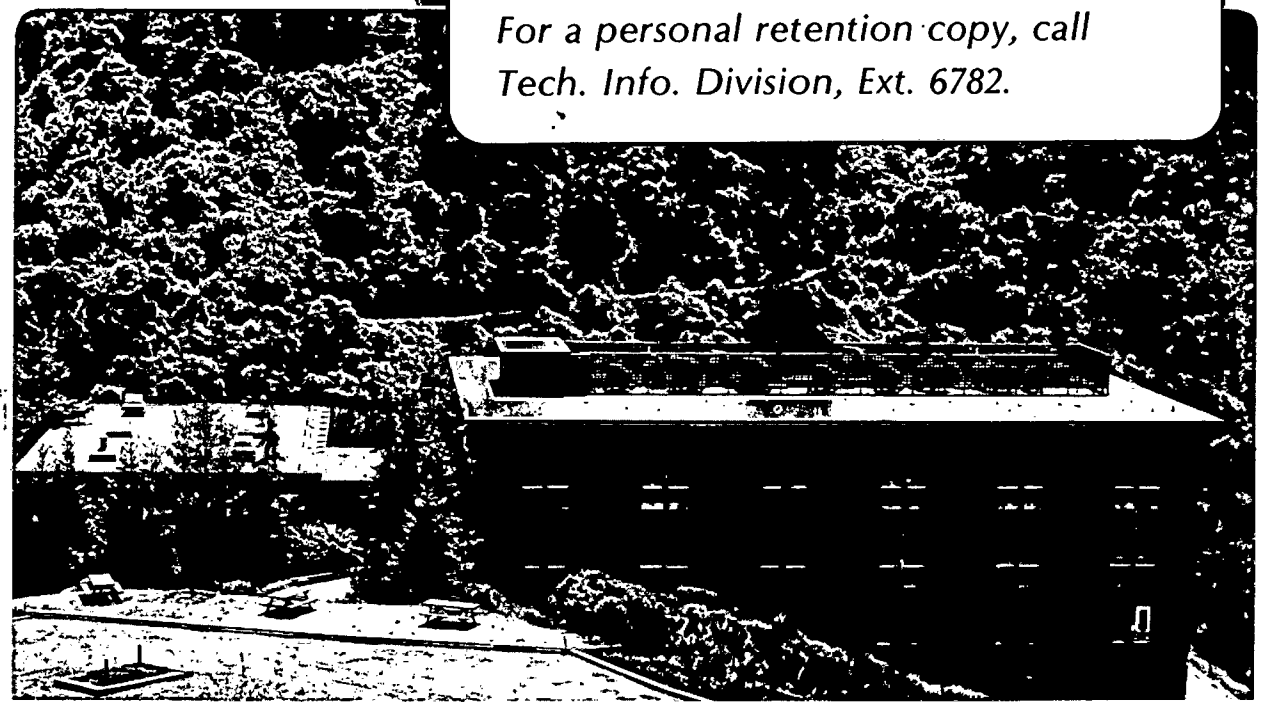

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Transient Stimulated Raman Scattering in High Laser Depletion and its Effects on Vibrational Dynamics Experiments

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Abstract

The progress of laser depletion and Stokes growth in Transient Stimulated Raman Scattering (TSRS) is investigated using a Rayleigh scattering technique. High laser depletion is found to dominate the behavior of TSRS under conditions relevant to excite-and-probe vibrational dynamics experiments. The results are used to explain discrepancies between recent vibrational dephasing experiments. Implications of the results on both energy relaxation (T_1) and phase relaxation (T_2) experiments utilizing TSRS excitation are discussed.

I. Introduction:

Picosecond excite-and-probe techniques are powerful tools for the study of ultrafast vibrational dynamics[1]. Transient Stimulated Raman Scattering (TSRS) has played a central role in many of these experiments as the source of vibrational excitation. Recent theoretical[2] and experimental[3,4] studies have revealed the importance of high depletion of the excitation laser pulse on experimental results. These results are not surprising in view of the dramatic differences between the low and high laser depletion behaviors of TSRS[2,5,6,7].

The proposed role of high laser depletion in excite-and-probe experiments raises two important questions: 1) How general is high laser depletion in the vibrational excitation process under typical experimental conditions? 2) How does high laser depletion affect vibrational relaxation experiments? In attempting to answer these questions, a technique has been developed which utilizes spontaneous Rayleigh scattering to observe directly the Stokes growth and laser depletion within the liquid Raman cell. By imaging the Rayleigh scattering intensity of the laser or Stokes pulses on an optical multichannel analyzer, a picture of the laser and stimulated Stokes pulse energies throughout the cell is obtained.

Using Rayleigh scattering, the progress of laser depletion and Stokes growth as a function of laser energy, wavelength, focal length, and path length in various liquids has been studied. The results reveal several characteristic properties of TSRS in low and high laser depletion. High laser depletion is found to dominate the behavior of TSRS under conditions relevant to vibrational dynamics experiments. The implications of these results on the design and interpretation of vibrational relaxation experiments are discussed.

II. Experimental:

Single pulses were extracted from the 2nd to 8th position in the rising edge of pulse trains emitted from a passively mode-locked Nd:glass laser[8]. The pulses were amplified and compressed in a saturable absorber dye cell (Eastman 9860). The resulting pulses had energies of approximately 1 to 10 mJ. The frequency doubled 530.6 nm laser pulses had temporal widths of about 7 psec and bandwidths of 5.0 ± 1.2 cm^{-1} [4]. These conditions correspond to those typically used in vibrational dephasing experiments[4].

A schematic of the optical set-up is shown in Fig. 1. The laser pulses were focused in a 10 cm liquid cell containing acetonitrile, acetone, or carbon tetrachloride using a variable focal length telescope. Relative laser energies before the cell as well as laser and Stokes pulse energies after the cell were detected using photodiodes (EG&G FOD-100, HP2-4203 642 PIN, and Rofin Ge 7460). A Bausch and Lomb 33-86-03 near IR monochromator was used to observe the Stokes pulse energies generated by 1.06 μm laser pulses. Fig. 1

An 1254 SIT (EG&G) optical multichannel analyzer(OMA) was used to monitor the progress of laser depletion and Stokes growth as a function of position in the liquid cell. The camera lens imaged the 10 cm liquid sample cell onto the 1.25 cm wide OMA screen. Rayleigh scattering of the laser pulse (530.6 nm) or stimulated Stokes pulse (628.4 nm) was observed using a Corning 4-76 or a Schott RG-610 filter, respectively. The total number of Rayleigh scattered 530.6 nm photons collected from the entire 10 cm cell by the 7×10^{-3} steradian collection optics was roughly 10^6 photons per mJ of laser energy. This estimate was made after correction for filter transmittance and assuming an OMA quantum efficiency of 5% at 530 nm.

In order to precisely determine the focal position and relative laser

intensity within the liquid cell, two photon fluorescence excited by the 530.6 nm laser pulse was detected by the OMA. For this purpose, a Coumarin 4 ethanol solution was placed in the 10 cm cell and a Ditric Optics 480 nm short pass interference filter was used.

III. Results:

Figure 2 shows the sharp onset of high laser depletion as a function of laser energy. This behavior was observed when either the 530.6 nm or 1.06 μm laser pulse was passed through a 10 cm acetonitrile Raman cell. The data in Fig. 2 was obtained by correlating the drop in the laser pulse energy after passage through the Raman cell with the Stokes signals measured after the cell. Thus the small Stokes signals obtained at low laser energies could be directly translated into the very low percent depletions shown in Fig. 1. The bunching of data in Fig. 2 reflects our attempt to maximize the number of shots in the 1% to 10% depletion region. Fig. 2

Figure 3 shows the progress of laser depletion and Stokes growth as a function of spatial location in the 10 cm acetonitrile Raman cell. These smoothed OMA Rayleigh scattering signals show the continuous spatial development of laser depletion and stimulated Stokes growth as the laser pulse travels through the cell. Previous observations of stimulated Stokes growth by Lewis and Knudtson utilized an array of beam splitters within the liquid cell[9,10]. Fig. 3

The Rayleigh scattered laser amplitudes on the left-hand side of the curves in Fig. 3(a) measure the energy of the incident laser pulse. The lowest curve in Fig. 3(a) represents a nondepleted laser pulse. At higher laser energy, the laser pulse is dramatically depleted during its passage

through the cell.

Figure 3(b) shows the growth of the stimulated Stokes pulses for laser pulse energies comparable to those in Fig. 3(a). The lower Rayleigh scattering cross section and OMA quantum efficiency at the Stokes wavelength resulted in a higher signal-to-noise ratio and a background of about 0.6 on Fig. 3(b). The curves in Figs. 3(a) and 3(b) are representative of the range of behavior which was observed.

Changing the effective focal length and the position of the focal region in the Raman cell had little effect on the high laser depletion behavior shown in Fig. 3. With effective focal lengths between 135 cm and 450 cm, corresponding to focal positions ranging from the entrance window to 60 cm beyond the exit window of the Raman cell, the threshold for 10% laser depletion varied by at most a factor of three. The lowest threshold was observed when the laser beam was focused near the center or towards the exit window of the cell with effective focal lengths of 200 cm to 350 cm. In all cases, similar behavior was observed after the threshold for high laser depletion was reached.

In order to demonstrate the generality of these results, the laser depletion behavior of TSRS under typical experimental conditions was also investigated in acetone and carbon tetrachloride. As shown in Fig. 4, the spatial rate of laser depletion and the threshold for high laser depletion were found to be essentially the same in the three liquids studied. Fig. 4

Previous measurements of the laser spectrum before and after the Raman cell indicate a broadening by less than a factor of two for the highly depleted laser pulses[4]. This broadening is consistent with the predicted shortening of the laser pulse due to TSRS saturation[2]. These results suggest that little if any self-focusing or self-phase modulation has taken

place under the experimental conditions.

IV. Discussion:

In the utilization of TSRS as a source of excitation in vibrational dynamics experiments, low laser depletion has generally been assumed[1]. This assumption has dictated the theoretical framework within which these experiments have been interpreted. The results of the current work as well as those of other recent studies[3,4] demonstrate that the assumption of low laser depletion is not necessarily justified.

A controversy has developed concerning the selectivity of excite-and-probe vibrational dephasing experiments, i.e. the ability of these experiments to measure a homogeneous dephasing time T_2 in an inhomogeneously broadened vibrational lineshape[2,3,4,11]. The discussion has centered around recent experimental measurements, by Kaiser and coworkers[11], of vibrational dephasing times under reported low laser depletion conditions. These recent measurements have produced nonselective results which are inconsistent with their previous, apparently selective, results also obtained under reported low depletion conditions[12,13,14]. Although they suggested that "accidentally" longer pulses and higher Stokes conversions might have been responsible for their earlier results, their conclusion was that the measurement of the homogeneous dephasing time T_2 in an inhomogeneously broadened lineshape is not possible using TSRS techniques.

A recent general theory of picosecond excite-and-probe vibrational dephasing experiments by George and Harris[2] suggests that the extent of laser depletion plays a critical role in the interpretation of experimental results. In low laser depletion, this theory reveals that very little

selectivity is possible. On the other hand, high laser depletion conditions lead to enhanced selectivity. This enhanced selectivity allows the homogeneous vibrational dephasing time T_2 in an inhomogeneously broadened lineshape to be measured to a high degree of accuracy.

These new theoretical results appear to resolve the discrepencies between many of the earlier vibrational dephasing experiments. The selective behavior observed in many previous experiments[1,3,4,12-17] can be explained if these experiments were actually performed in high laser depletion where high selectivity is predicted[2]. This suggestion is not unreasonable considering the difficulty of maintaining laser depletion at a low level (Fig. 2). On the other hand, the more recent nonselective results of Kaiser and coworkers[11] are consistent with their claimed low laser depletion conditions and the predicted low selectivity in low laser depletion[2].

The results shown in Fig. 3(a) indicate that the extent of overall laser depletion is a function of cell length. Very little depletion was observed over the first few centimeters of the cell under the wide range of focal geometries and incident laser energies employed in this study. This behavior might explain the previously observed dependence of selectivity on the Raman cell length[1,12]. Selective or nonselective results were obtained when long (5-10 cm) or short (1 cm) Raman cells were used, respectively. Because longer cells display higher laser depletion, the observed selectivity dependence is in agreement with the predicted high selectivity in high laser depletion and low selectivity in low laser depletion[2].

We note, however, that even when the overall laser depletion is maintained at about 5 percent, a much higher depletion may exist at the center of the laser pulse. We have calculated the radial dependence of laser depletion based on a Gaussian radial intensity profile and the laser depletion

behavior determined by George and Harris[2]. The results of these calculations indicate that when the laser pulse as a whole has reached 5% depletion, the center of the laser pulse has already depleted by more than 30%. Consequently, local high depletion of the laser is expected to occur even under relatively low overall depletion conditions. Although such local high depletion may not be sufficient to lead to substantial selectivity, its presence indicates that a general theory including both high and low laser depletion must be used to interpret experimental results.

The high laser depletion behavior observed in Fig. 3 also has an important bearing on vibrational energy (T_1) experiments. Lewis and Knudtson have argued that in high laser depletion, the position of maximum vibrational excitation in the liquid cell may depend on laser intensity[9,10]. This is expected to occur because the position of peak vibrational excitation corresponds roughly with the point where the slope of the Stokes growth as a function of position in the cell is greatest. Figure 3(b) clearly shows that the greatest slope in the Stokes growth does not occur at the end of the 10 cm cell.

Our calculations based on the numerical results of George and Harris[2] suggest that the vibrational population density within the Raman cell is a complicated function of the radial intensity distribution of the laser pulse. In high laser depletion, the position of greatest population density fluctuates with the shot-to-shot intensity variations of the laser pulses. Consequently, the probability of overlap between the probe pulse and the excited population is greatly reduced by high laser depletion when utilizing the usual non-collinear probing geometry in T_1 experiments[18-22].

V. Conclusion:

High laser depletion has been found to dominate the behavior of TSRS under conditions typical of those used in excite-and-probe vibrational dynamics experiments. The results appear to be independent of the particular liquid, excitation wavelength or focal geometry used. A complete reevaluation of both the design and interpretation of vibrational dynamics experiments utilizing TSRS excitation is required. Such a reinterpretation of vibrational dephasing experiments has recently been performed[2].

VI. Acknowledgements:

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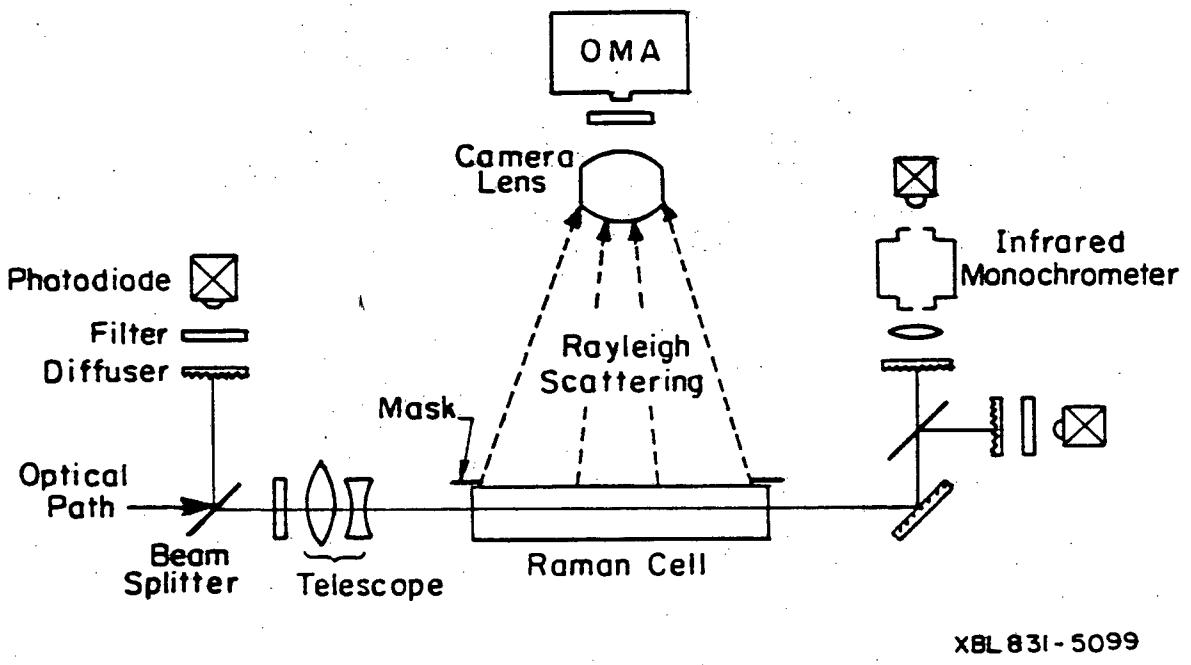
FIGURE CAPTIONS

FIG. 1. Experimental set-up for measuring laser depletion and Stokes growth as a function of position in the liquid Raman cell using Rayleigh scattering.

FIG. 2. Percent depletion of the laser pulse after passing through a 10 cm acetonitrile cell: (a) 530.6 nm laser wavelength; (b) 1.06 μm laser wavelength.

FIG. 3. A representative sampling of smoothed Rayleigh scattering profiles from the 10 cm acetonitrile cell. As the laser propagates from left to right through the cell: (a) illustrates the dramatic depletion of the larger incident laser pulses while (b) illustrates the associated growth of stimulated Stokes pulses.

FIG. 4. Actual Rayleigh scattering profiles of the laser pulse versus position in the liquid cell for three liquids. In (a), (b) and (c), the laser intensity was below the threshold for high laser depletion. In (a'), (b') and (c'), the laser intensity was above the threshold for high laser depletion. These profiles display typical experimental signal-to-noise.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Camera Lens
Photodiode
Filter
Diffuser
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Beam Splitter
Telescope
Mask
Rayleigh Scattering
Raman Cell
Infrared Monochrometer
XBL831-5099

Figure 1

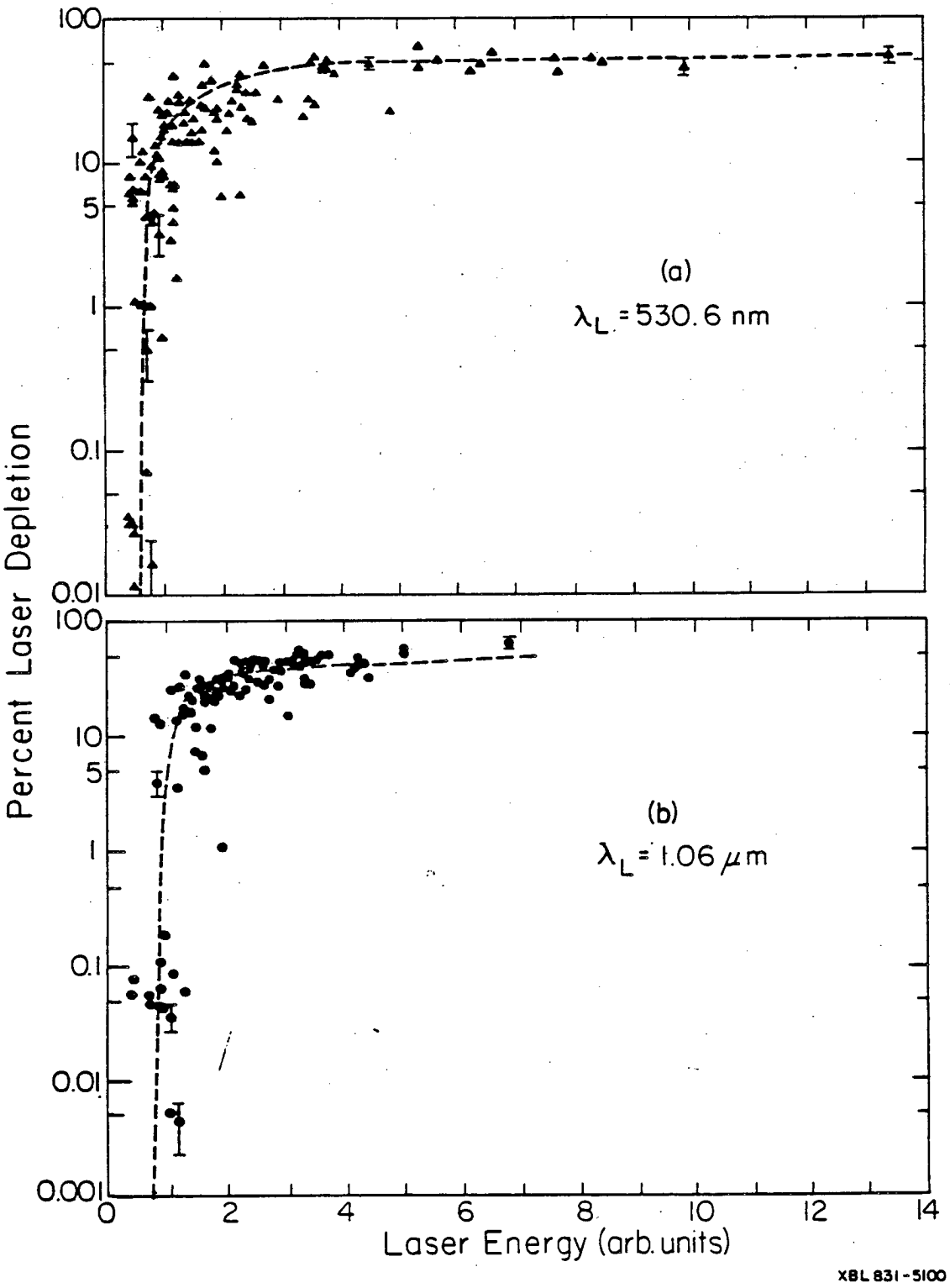
Percent Laser Depletion
100
10
5
1
0.1
0.01
(a)
λ_L = 530.6 nm
100
10
5
1
0.1
0.01
0.001
(b)
λ_L = 1.06 μm
0
2
4
6
8
10
12
14
Laser Energy (arb. units)
XBL 831-5100

Figure 2

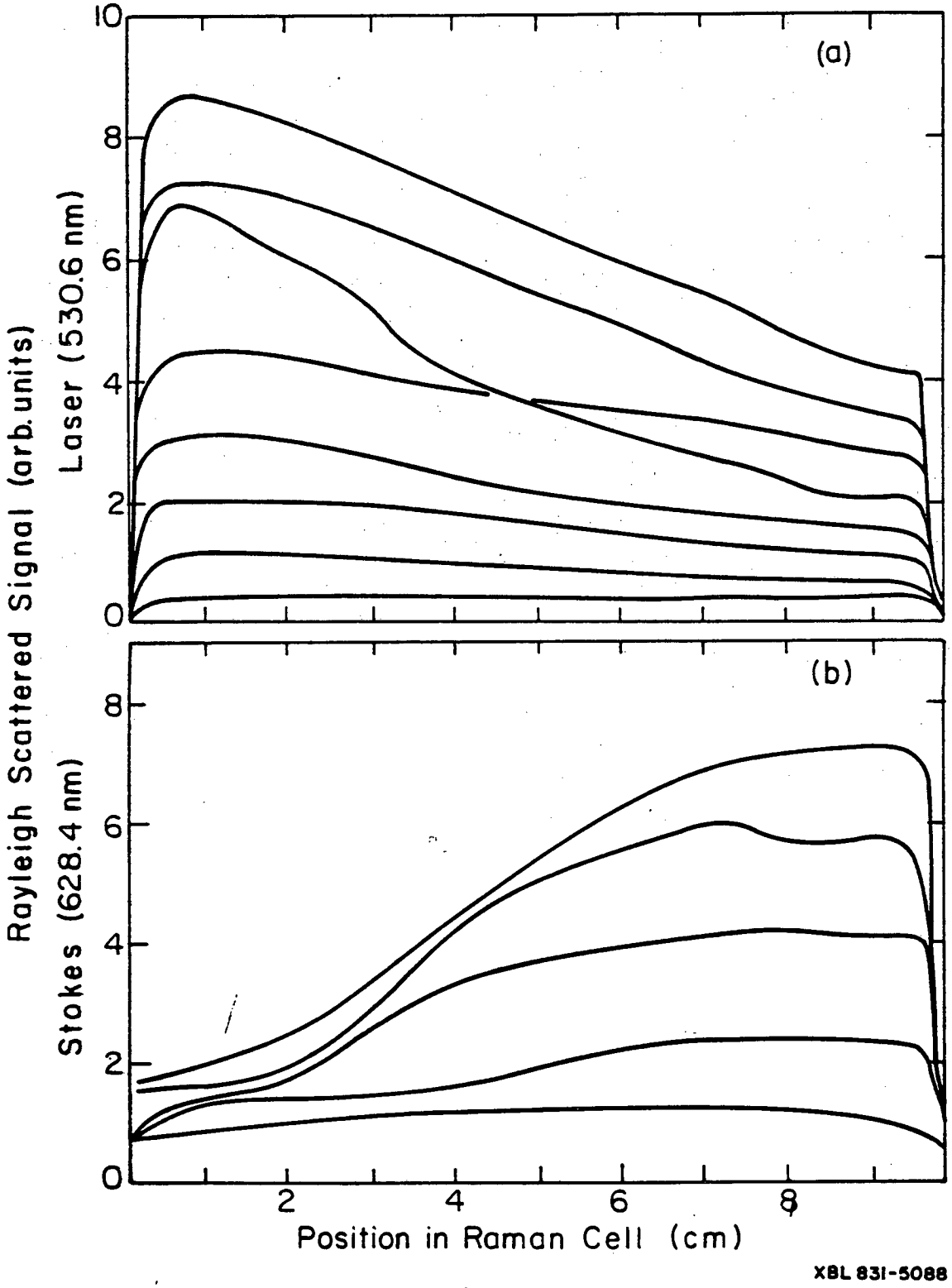
(a)
(b)
Rayleigh Scattered Signal (arb.units)
Laser (530.6 nm)
Stokes (628.4 nm)
Position in Raman Cell (cm)
0
2
4
6
8
10
XBL 831-5088

Figure 3

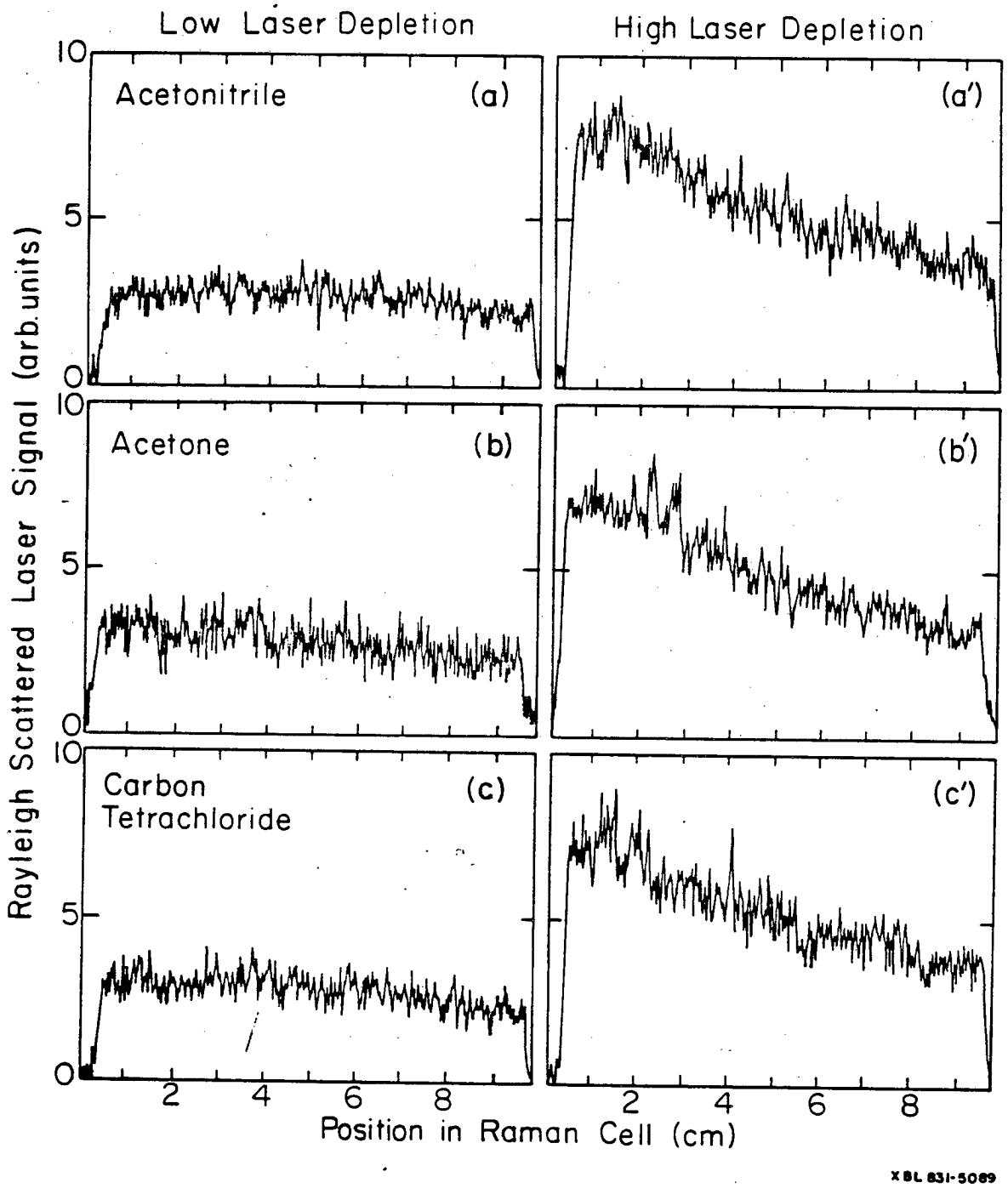
Low Laser Depletion
High Laser Depletion
Acetonitrile
(a)
(a')
Acetone
(b)
(b')
Carbon Tetrachloride
(c)
(c')
Rayleigh Scattered Laser Signal (arb.units)
Position in Raman Cell (cm)
0
5
10
2
4
6
8
XBL 831-5089

Figure 4

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