

## PICOSECOND SPECTROSCOPY USING THE INVERSE RAMAN EFFECT

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Spectroscopy on a picosecond time scale is shown to be feasible by a new technique. Inverse Raman spectra are obtained when the intense continuous spectrum of a self-phase modulated picosecond pulse is coincident in liquid and solid samples with an intense 5300 Å picosecond laser pulse.

Recently two spectroscopic measurement techniques have been extended into the nanosecond time domain - inverse Raman spectroscopy [1-4] and flash photolysis [5]. We report observation of inverse Raman spectra with picosecond laser pulses - an improvement of four orders of magnitude over the previous best time resolution. This improvement is important because it permits the measurement of short lifetimes.

Jones and Stoicheff [1] first demonstrated the inverse Raman effect. When a 6943 Å 30 nsec pulsed ruby laser beam and a narrow continuum provided by stimulated anti-Stokes Raman scattering in toluene are simultaneously passed through a benzene sample, absorption is observed in the continuum at the frequency of the anti-Stokes Raman line of benzene. McLaren and Stoicheff [3] showed that the short lived spontaneous fluorescence from Rhodamine B or 6G provides a suitable continuum for inverse Raman spectroscopy and suggested that by selecting different dyes a wide spectral range could be explored. The time resolution in their experiment is limited by both the duration of the laser pulse (40 nsec) and the fluorescence lifetime of the dyes (4 nsec).

Recently we showed [6] that when a 5300 Å picosecond pulse of high intensity passes through a solid or liquid, self-focusing can occur and the pulse becomes self-phase modulated leading to spectral emission over the entire visible region\*. This continuum is suitable for Raman spectroscopy

and flash photolysis and has two distinct advantages over the latest technique presented by McLaren and Stoicheff [3]: (i) the duration of the self-phase modulated emission continuum and the laser pulse is only 4 psec, an improvement in time resolution of  $\approx 10^4$  which should allow observation of new short lived species and measurement of short lifetimes; (ii) a spectral region covering *thousands* of wavenumbers can be scanned in a single shot.

We observe inverse Raman spectra with the 4 psec self-phase modulated emission as indicated by absorption in the continuum at the anti-Stokes frequencies in benzene, carbon disulfide, methanol, liquid nitrogen and calcite. We have also observed new absorptions on the Stokes side of the 5300 Å line in carbon disulfide, benzene and toluene.

Experimentally a modelocked Nd:glass laser emits picosecond pulses at 1.06  $\mu$  which are converted to 5300 Å picosecond pulses by second harmonic generation in a KDP crystal. The 5300 Å pulses are then focussed with a 20 cm focal length lens into a 5 cm sample of borosilicate BK-7 glass producing a self-phase modulated continuum. The beam measures 400  $\mu$  in diameter at the entrance and exit faces of the BK-7 glass and 350  $\mu$  in diameter at the center. A fraction of the 5300 Å light is self-focussed in the BK-7 glass into filaments, and the light emerging from the filaments is self-phase modulated and emitted in the region from 4000 Å to 7000 Å. Since the dispersion is small in the BK-7 glass, the 5300 Å pulse which still contains most of the energy emerges from the glass coincident in time with the frequency swept part of the pulse. The swept pulse and the intense laser pulse pass into a sample of 5 cm length, and the emerging light is

\* We have extended the spectral emission between 2900 Å and 8000 Å by using a 22 cm long sample of supracil quartz.

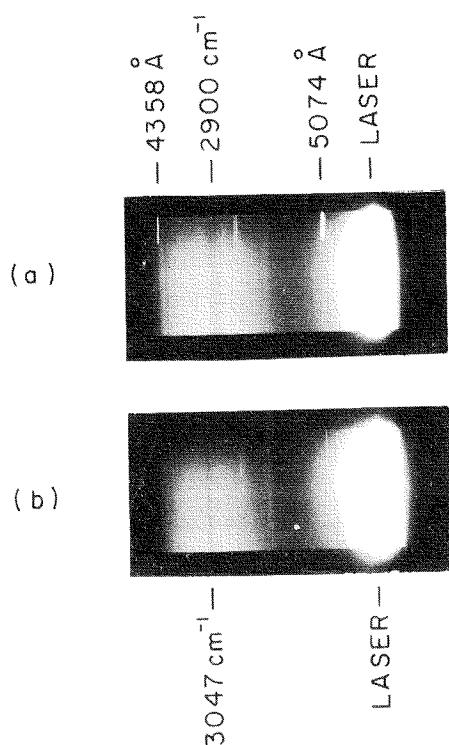


Fig. 1. The anti-Stokes absorptions in (a) methanol at 2837 and 2942  $\text{cm}^{-1}$ , (b) benzene at 3047  $\text{cm}^{-1}$ ,

collected by a lens and imaged into either a 3/4-m Jarrell Ash f/6.5 or 1/2-m Jarrell Ash f/9 spectrograph. This experimental arrangement is chosen because the continuum generated in the glass is much more intense than any continuum generated in the samples themselves, so that the absorption takes place in the continuum generated in the BK-7 glass. Also the continuum generated by glass has a smooth intensity variation since there are no stimulated Raman lines emitted and no absorptions in the visible region. This technique was used exclusively for taking inverse Raman spectra on the anti-Stokes side in liquid carbon disulfide, benzene, nitrogen, methanol and calcite.

Each laser pulse has a power of 0.5 GW, and  $\approx 10^{-2} - 10^{-3}$  of the laser light energy emerges in the self-phase modulated continuum distributed over 10000  $\text{cm}^{-1}$ . Most spectra are obtained on one laser shot. In observations of Stokes spectra 3-67 and 3-68 Corning filters are used to prevent the 5300 Å direct laser light from entering the spectrograph, while on the anti-Stokes side of the spectra 5-60 or 5-61 or 1-64 filters attenuate

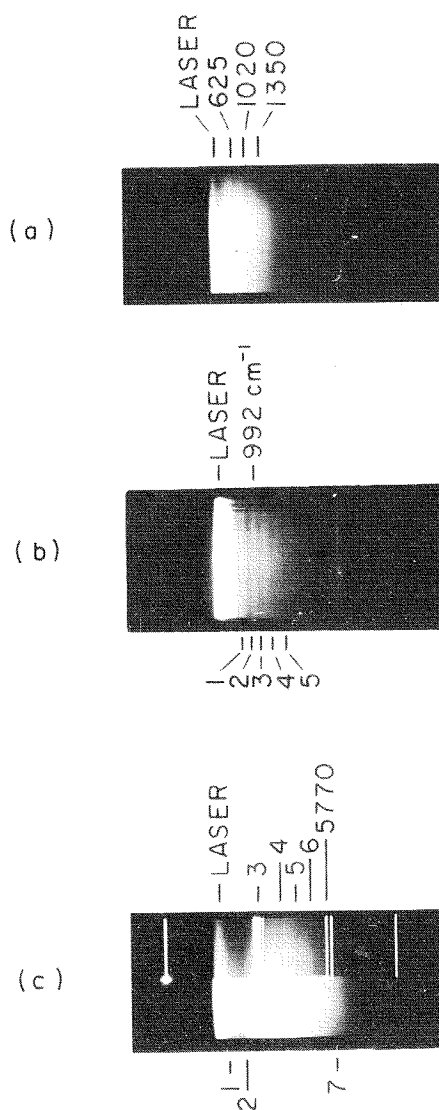


Fig. 2. Stokes absorptions in (a) carbon disulfide, (b) benzene, (c) toluene; the top half of the spectra in toluene is attenuated 3 $\times$ .

the laser light. Spectra are taken on Polaroid 3000 speed film.

An alternative method of obtaining inverse Raman spectra, which we used to obtain Stokes absorption spectra in benzene and carbon disulfide, is to let the picosecond pulse itself generate the self-phase modulated continuum in the sample. The laser beam is focussed into the sample directly, and a ground glass screen is placed after the

sample. Light emanating from the ground glass screen is imaged onto the grating of the spectrograph with a 5 cm focal length lens.

Samples are deliberately kept short to avoid dispersion problems. The pulse at 5300 Å must arrive simultaneously with the continuum in order to have absorption. When a 10 cm long quartz sample is substituted for the borosilicate glass, no absorption is observed at the 3047 cm<sup>-1</sup> line in benzene simply because the sweep generated in the quartz becomes sufficiently separated spatially from the laser pulse as a result of dispersion in the longer quartz sample.

Fig. 1 shows inverse Raman spectra on the anti-Stokes side in the BK-7 glass continuum due to the 3047 cm<sup>-1</sup> line of benzene and a broader absorption due to the 2837 cm<sup>-1</sup> and 2942 cm<sup>-1</sup> lines of methanol. We have also observed the anti-Stokes absorptions due to the 1086 cm<sup>-1</sup> line in calcite, 2331 cm<sup>-1</sup> line in liquid nitrogen, and 656 cm<sup>-1</sup> lines in CS<sub>2</sub>\*. Fig. 2a shows Stokes absorptions [4] in carbon disulfide at 625 cm<sup>-1</sup>, 1024 cm<sup>-1</sup> and 1352 cm<sup>-1</sup>. Fig. 2b shows the new unreported absorptions on the Stokes side in benzene at 507 cm<sup>-1</sup>, 851 cm<sup>-1</sup>, 1174 cm<sup>-1</sup>, 1489 cm<sup>-1</sup> and 1832 cm<sup>-1</sup> and also an emission at 992 cm<sup>-1</sup> which becomes very intense on increasing the laser power. Fig. 2c shows Stokes absorptions at 138 cm<sup>-1</sup>, 352 cm<sup>-1</sup>, 616 cm<sup>-1</sup>, 901 cm<sup>-1</sup>, 1167 cm<sup>-1</sup>, 1408 cm<sup>-1</sup> and 1597 cm<sup>-1</sup> in toluene. The accuracy of the Stokes measurement is limited to ± 30 cm<sup>-1</sup> because the laser linewidth is 100 cm<sup>-1</sup>.

The Stokes absorptions in CS<sub>2</sub> are probably due to an absorption at a fundamental (656 cm<sup>-1</sup>) and absorption at combination frequencies - 656 + 397 cm<sup>-1</sup> and 656 + 656 cm<sup>-1</sup>. Because benzene is a complex polyatomic molecule having

\* The appearance of these particular anti-Stokes absorptions was erratic. The 2331 cm<sup>-1</sup> line was observed once, the 1086 cm<sup>-1</sup> and 656 cm<sup>-1</sup> lines occasionally, the 992 cm<sup>-1</sup> line in benzene - never. The reason for this difficulty is not known, but we note that spontaneous Raman measurements show that all these lines are sharp.

twenty normal vibrations, some of which are inactive, it becomes difficult to assign a given absorption with certainty to either an active mode, inactive mode, or any combination of these. Three possible explanations are listed for the newly observed benzene Stokes absorptions: 1) three frequencies at 851, 1174 and 1489 cm<sup>-1</sup> correspond to active benzene vibrations while the remaining two may be combination frequencies; 2) inactive Raman modes have become active [4] under the influence of the intense electric field; theoretical calculations of inactive mode frequencies [7] agree with four of the observed frequencies (507, 1174, 1489 and 1832 cm<sup>-1</sup>); 3) an intriguing possibility is that a new species which decays rapidly has been formed and only is observed on a picosecond scale.

In conclusion we have demonstrated that the frequency swept pulses which are generated upon passage of 5300 Å picosecond pulses through materials is a suitable source for picosecond spectroscopy.

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