Enhancement of the stimulated Raman scattering of benzene, acetonitrile and pyridine

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Abstract. In this work we used the second harmonic of Nd:YAG laser to observe stimulated Raman scattering (SRS). SRS was observed on benzene, acetonitrile and pyridine using a single shot laser. The SRS radiation is very intense due their laser characteristics, and it is possible to observe several harmonics of different vibrational modes to each molecule studied here.

1. Introduction

Raman spectroscopy is a technique used in vibrational studies; this method gives complementary information to FTIR. Raman spectroscopy is limited by very low intensity of normal Raman scattering, however, when is used laser sources focused on the sample; it is possible to observe Stimulated Raman scattering (SRS) [1-6]. SRS is well-known nonlinear Raman phenomenon in which photon energy is transferred from an anti-Stokes (AS) pulse to a Stokes (S) pulse when the frequency difference matches a Raman vibrational mode. Stimulated processes, nonlinear phenomena amplify the ordinarily weak Raman effect to the point where it is easily visible to the eye [1, 3, 6]. By observing this process, it is possible to examine some details about the vibrational energy levels of the scattering molecules and gain insight into the special ways that a very intense radiation field can interact with a molecule. However, SRS is used most widely for conversion of the frequency of laser radiation to the long-wavelength region of the spectrum, which makes it possible to design new laser radiation sources based on SRS for regions of the spectrum where using conventional laser output is very difficult to achieve. Several studies on nonlinear optical phenomena of liquids under strong laser irradiation have shown anomalous enhancement of stimulated Raman scattering (SRS). This enhancement is explained by the phase transition from liquid to plasma state [2, 4, 7, 8]. Moreover SRS spectroscopy has been used as a highly sensitive spectroscopic tool for chemical analyses in the condensed and gas phases [5]. In 1980, Heritage and Allara studied SRS detection of a single molecular monolayer [9]. While Volkmer et al. [10] demonstrate SRS as a contrast mechanism for label-free optical microscopy, which provides readily interpretable and background-free chemical
image contrast. In addition, they show that SRS is linearly proportional to the Raman response and is inherently insensitive to any non-resonant background contributions.

2. Experimental

A schematic diagram of the experimental setup is shown in the figure 1. The second harmonic of a Nd:YAG pulsed laser beam (532 nm, 10 Hz and 8 ns/pulse, The spatial profile of the beam is a Gaussian distribution) was focused with a short (50 mm) focal length lens into a cell containing benzene, acetonitrile or pyridine (optical path of the cell was of 50 mm). The excitation power was 10 mJ/pulse and the power density at the beam waist was estimated as 6.4 \times 10^9 \text{W cm}^{-2} at most from calculation of the beam with a Gaussian spatial profile. The power was adjusted until do not observe laser-induced plasma y the liquid. Raman-shifted laser light (SRS) was observed in the forward direction with respect to the excitation beam axis using a compact spectrometer (Ocean Optics HR4000). To attenuate the laser radiation we use a Nocht filter.

![Figure 1. Experimental setup.](image)

3. Results and discussion

In Stimulated Raman scattering (Figure 2), the amplified radiation emerges as a coherent beam coincident with the direction of the incident laser radiation. The amplification process sets up intense molecular vibrations in the sample at a frequency corresponding to the strongest Raman transition for the molecule.

![Figure 2. SRS Process. a) Normal SRS; b) Harmonics generations.](image)
Figure 3 show typical SRS spectra of three compounds studied here. Despite spectra was obtained using single laser shot, Raman shifted signals are very intense due their laser characteristics. Also, it is possible to observe with high intensity the anti-Stokes lines.

| Vibrational modes | Wavelength (nm) | SRS Shifts (cm⁻¹) |
|-------------------|----------------|------------------|
| Nd:YAG SH         | 532.1          | ---              |
| Benzene Stokes(v₁) | 561.8          | 994.93           |
| Stokes(2v₁)       | 595.1          | 1991.0           |
| Stokes(3v₁)       | 632.5          | 2984.6           |
| Stokes(4v₁)       | 675.0          | 3980.0           |
| Stokes(v₂)        | 635.6          | 3061.7           |
| Stokes(2v₂)       | 789.3          | 6125.4           |
| a-Stokes(v₂)      | 505.4          | 993.40           |
| a-Stokes(2v₂)     | 481.6          | 1973.7           |
| Acetonitrile      |                |                  |
| Stokes(v₁)        | 630.8          | 2942.0           |
| Stokes(2v₁)       | 774.7          | 5886.7           |
| Stokes(3v₁)       | 1003.4         | 8828.8           |
| a-Stokes(v₁)      | 461.0          | 2897.1           |
| a-Stokes(2v₁)     | 405.2          | 5884.3           |
| Pyridine Stokes(v₁) | 561.7          | 991.8            |
| Stokes(2v₁)       | 594.9          | 1985.3           |
| Stokes(v₁2)       | 635.7          | 3064.2           |
| a-Stokes(v₁)      | 505.4          | 991.4            |

Figure 3. SRS spectra of Acetonitrile, Benzene and Pyridine.
The Table 1 shows SRS line positions and shifts found for Benzene, Acetonitrile and Pyridine. In acetonitrile is observed the vibrational mode n1 corresponding to CH symmetrical stretch ($A_1$), in this molecule is possible to observe two anti-Stokes lines and three Stokes lines (the second anti-Stokes lines and second and third Stokes lines are due by the process shown in figure 2b), in benzene the in-plane, ring-breathing mode ($\nu_2$) is especially intense, but the $\nu_1$ symmetric CH stretch produce also stimulated Raman scattering. Both lines present seconds harmonics. In pyridine, we observed SRS in two strongest vibrational modes; ring-breathing mode ($\nu_1$) and trigonal ring breathing mode, ($\nu_{12}$).

In this conditions was possible observe laser lines using SRS in liquid states of simple molecular system. Taking in account the differences in intensity and frequencies of SRS, this process could be used as analytical technique.

4. Conclusion

We found enhancement of the SRS of the benzene, acetonitrile and pyridine with laser characteristics, this enhancement is possibly due generation of plasma just after the scattering phenomena. Enhancement of the SRS allowed observing several harmonics of different vibrational modes of molecules studied here. According with this, Stimulated Raman scattering can be used in a variety of applications, including production of coherent light of varying frequencies and the transfer of a signal from one laser source to another having a different frequency. Also, SRS may be used as an analytical technique for identification of different compound.

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References

[1] Melin S and Nibler J W 2003 J. Chem. Ed. 80 1187
[2] Yui H, Nakajima T, Hirao K and Sawada T 2003 J. Phys. Chem. A 107, 968
[3] Grant C A and Hardwick J L 1997 J. Chem. Ed. 74 318
[4] Yui H, Nakajima T, Yoneda Y and Sawada T 1999 Phys. Rev. Lett. 82 4110
[5] Zuo J, Tian Y–J, Chen J, Wang Y–C, Gao S–Q, Lu G–H and Li Z–W 2008 Appl. Phys. B 91 467
[6] Borman S A 1982 Anal. Chem. 54 1021A
[7] Yui H, Kitamori T and Sawada T 1999 Chem. Phys. Lett. 306 325
[8] Liu D, Shi J, Ouyang Min, Chen X, Liu J and He X 2009 Phys. Rev. A 80, 033808
[9] Heritage J P and Allara D L 1980 Chem. Phys. Lett. 74 507
[10] Nandakumar P, Kovalev A and Volkmer A 2009 New J. Phys. 11 033026