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Editors
K.B. Eisenthal R.M. Hochstrasser W. Kaiser
A. Laubereau

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A Picosecond Raman Technique with Resolution Four Times Better than Obtained by Spontaneous Raman Spectroscopy

W. Zinth, M.C. Nuss, and W. Kaiser

Physik Department der Technischen Universität München
D-8000 München, Fed. Rep. of Germany

A new Raman technique is presented which allows to observe a Raman transition with a bandwidth smaller than the common spontaneous Raman line-width.

This technique is based on short excitation and prolonged interrogation (SEPI) of molecular states /1,2/. During the short and transient excitation process the molecules are driven at the difference frequency $\nu_D = \nu_1 - \nu_2$ by two pulses of frequency ν_1 and ν_2. Raman transitions which are close to the frequency ν_D become coherently excited with amplitudes Q_i. This material excitation persists when the two pumping pulses have left the sample. After the excitation the molecules vibrate with their individual resonance frequencies and the coherent amplitudes Q_i decay exponentially with the time constants T_{2i}. A third delayed probe pulse interacts with the coherently vibrating molecules and generates a Stokes spectrum of the freely relaxing material excitation.

The crucial point of the transient excited Raman spectroscopy discussed here is the narrow Stokes spectrum produced by the long third pulse. Only molecules vibrating in phase contribute to the coherent Stokes light. Molecules which have suffered collisions are out of step and are not observed subsequently. For Gaussian shaped probing pulses the spectral width of the observed Stokes bands equals the width $\Delta\nu_L$ of the interrogating third pulse /1,2/. With long probing pulses of duration $t_p > 1.4\ T_{2i}$ the SEPI resolution will be better than the resolution of spontaneous Raman scattering.

The experiments on SEPI spectroscopy are performed using a picosecond Nd-glass laser system /2/. The second harmonic frequency ν_1 is used for one pumping and the probing pulse. The second pump frequency ν_2 is generated via transient stimulated Raman scattering in a generator cell.

Experimental results on liquid cyclohexane in the frequency range 2850 cm^{-1} to 2940 cm^{-1} are shown in Fig.1. Fig.1a shows the emission band-widths of the liquids employed to generate pulses at ν_2. The spontaneous polarized Raman spectrum of C_6H_{12} is shown in Fig.1b. Between the three strong CH-stretching modes one encounters a diffuse spectrum due to overlapping overtones or combination bands. Transition frequencies found in SEPI spectroscopy are marked with the vertical lines.

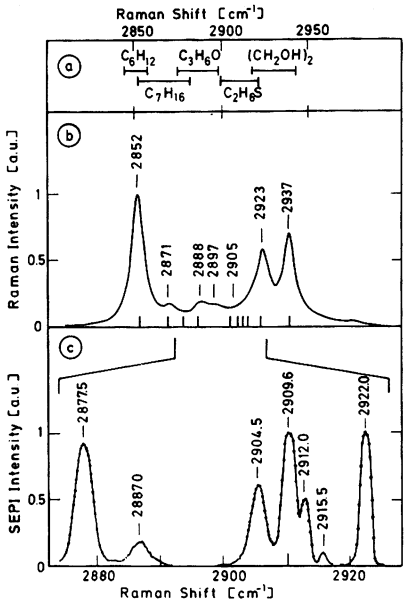

Fig.1 Experimental results of SEPI spectroscopy of C_6H_{12}. (a) Frequency ranges of the various Raman generators liquids used in the experiment. (b) Polarized spontaneous Raman spectrum of of C_6H_{12} recorded with a resolution of 1 cm^{-1}. The frequency positions of the resonances found in SEPI spectra are marked with vertical lines. (c) Three SEPI spectra taken with different generator liquids. New Raman lines are detected and the spectral resolution is improved. (Note, the frequency scale of (c) is 3.7 times larger than the one of (b).)

In Fig. 1c we show three SEPI spectra on an expanded scale (factor 3.7). Each spectrum was obtained by a single laser shot. On the r.h.s. we present the sharp SEPI band corresponding to the CH-stretching mode at 2923 cm^{-1}. We note that the SEPI band is considerably narrower than the corresponding band in the spontaneous Raman spectrum. The SEPI spectrum in the center shows four Raman transitions between 2905 cm^{-1} and 2916 cm^{-1}. Lines as close as 2.5 cm^{-1} are clearly resolved. In spontaneous Raman spectra the four transitions are hidden under the wing of the strong Raman band at 2923 cm^{-1} and cannot be detected. Fig.1c, l.h.s.,shows a SEPI spectrum of the frequency range 2875 cm^{-1} to 2890 cm^{-1}. We find two distinct Raman bands at 2877.5 cm^{-1} and 2887 cm^{-1}. The band at 2877.5 cm^{-1} has never been reported on previously. It is buried in the diffuse part of the conventional Raman spectrum.

The following points are relevant for the application of the SEPI technique: (i) The frequency positions of the observed Raman lines are independent of the excitation conditions since we observe freely relaxing molecules. (ii) In SEPI experiments the exciting and interrogating pulses should not overlap temporarily in order to avoid the generation of a coherent signal via

the non-resonant four-photon parametric process. (iii) SEPI spectra taken for different delay times allow an estimate of the dephasing times T_{2i}. (iv) The frequency precision of the generated Stokes spectrum depends upon the frequency stability of the interrogating pulse. For highest accuracy the frequency ν_1 has to be measured simultaneously with the SEPI spectrum. (v) The scattering process may also be performed on the anti-Stokes part of the spectrum. The disturbing interference found in stationary CARS spectroscopy does not occur for the delayed probing used with SEPI spectroscopy.

The data presented here give convincing evidence of the potentiality of the short excitation and prolonged interrogation spectroscopy; new Raman lines are readily observed and vibrational energies are determined with improved accuracy.

References

1 W. Zinth, Optics Commun. 34 (1980) 479
2 W. Zinth, M.C. Nuss, and W. Kaiser, Chem. Phys. Lett. 88, (1982) 257