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A NEW RAMAN TECHNIQUE OF SUPERIOR SPECTRAL RESOLUTION

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Raman-active vibrational modes are coherently excited by the transient stimulated Raman process. A subsequent delayed probe of relatively long duration interacts with the freely relaxing vibrations. Raman spectra are generated with higher resolution and more accurate peak positions than in conventional Raman spectroscopy. In liquid cyclohexane four new Raman lines were readily detected in the frequency range 2870–2920 cm^{-1}.

1. Introduction

In the past, infrared and Raman spectra have been a major source of information for the clarification of the structure of polyatomic molecules [1]. For a full spectral analysis one needs to know the frequencies of the normal modes and one likes to have numerous combination modes and overtones. An accurate knowledge of the band positions is of great importance for comparison with model calculations. With laser excitation sources and modern electronic detection techniques, the spectral resolution of conventional Raman spectra is determined by the linewidth of the vibrational states. In liquids linewidths are usually of the order of 10 cm^{-1} and, as a result, the resolution and precision of band positions is several wave numbers. The situation is critical in congested spectral regions where weak, unknown transitions might be buried under stronger Raman bands.

In this letter we describe a new Raman technique of improved spectral resolution. New Raman lines are readily detected in congested spectral regions and – quite important – the peak positions of Raman lines in liquids can be measured with unprecedented accuracy.

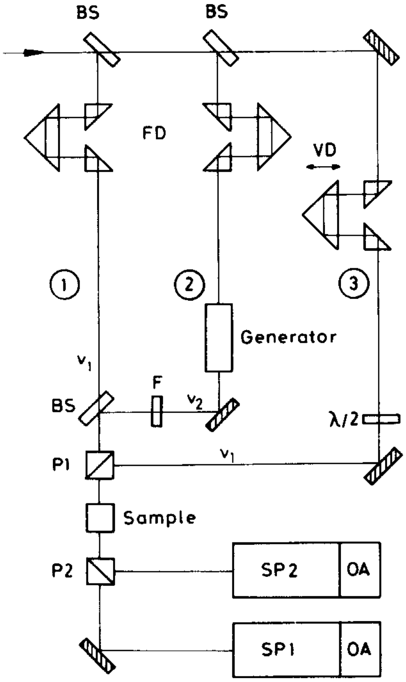

Fig. 1. Schematic of the experimental system used for the study of SEPI spectra of liquids. Beam splitters BS, variable and fixed delay lines VD and FD, polarizers P1 and P2, blocking filter F, spectrographs SP1 and SP2, used in conjunction with optical spectrum analysers OA.

2. Experimental

Fig. 1 shows a schematic of our experimental system. At the top left a single, frequency-doubled, pulse from a mode-locked Nd–glass laser system enters [2]. This pulse of frequency ν_1 = 18990 cm^{-1} and dura-

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tion 8 ps is split into three parts by two consecutive beam splitters. The pulse in beam 1 passes through the polarizer P1 and the sample but is blocked by the polarizer P2 in its straight path. In the center beam 2 of fig. 1 a new frequency ν_2 is produced in the generator by a stimulated Raman process. Changing the medium of the generator one readily obtains pulses of different frequencies ν_2. These pulses are blocked by the polarizer P2 and are spectrally monitored by spectrograph SP2. On account of the transient generation process the pulses of frequency ν_2 are shorter in duration than the incident pulses ν_1 by a factor of approximately three [3]. The two pulses of the beams 1 and 2 simultaneously enter the sample exciting molecular vibrations coherently via transient stimulated Raman scattering at a frequency $\nu_D = \nu_1 - \nu_2$. In the optical path 3 a delayed pulse with polarisation perpendicular to the pulses of 1 and 2 is produced. This third pulse interacts with the coherently excited volume of the sample producing a Stokes-shifted signal pulse. The latter passes the polariser P2 and is spectrally studied by a 2 m spectrograph SP1 and a cooled optical spectrum analyser OA. The system has a resolution of 0.2 cm^{-1} per channel and an absolute accuracy in the frequency scale of 0.4 cm^{-1}.

3. Principle of the new spectroscopic method

The technique presented here is based on short excitation and prolonged interrogation (SEPI) of molecular states [4]. During the short and transient excitation process the molecules are driven at the difference frequency $\nu_D = \nu_1 - \nu_2$ by the 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 even after the two pumping pulses have left the sample. After the excitation the molecules return to their individual resonance frequencies and the coherent amplitudes Q_i decay exponentially with their individual time constants T_{2i}. We recall that the molecules are driven with a wave vector $k_D = 2\pi(\nu_1/\mu_1 - \nu_2/\mu_2)$ where μ_1 and μ_2 are the refractive indices of the sample at the frequencies ν_1 and ν_2, respectively [5]. During the free relaxation process the different vibrations have individual wave vectors k_i. The third delayed probe pulse interacts with the coherently vibrating molecules with various wave vectors k_i 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. Molecules which vibrate freely for several dephasing times T_2 interact with the delayed, long, third pulse and give a sharp Stokes spectrum. The spectral width of the observed Stokes bands is determined by the spectral width $\Delta\nu_L$ of the interrogating third pulse [4,5]. In our experiments we worked with gaussian pulses of $t_p = 8$ ps duration which gives $\Delta\tilde{\nu}_L \approx 2\ \mathrm{cm}^{-1}$. We emphasize the distinction between the common spontaneous Raman spectrum and the SEPI technique. For molecules with homogeneously broadened Raman bands the spontaneous halfwidth $\Delta\nu$ (fwhm) is determined by the dephasing time T_2: $\Delta\nu = 1/\pi T_2 = 0.32/T_2$, while for the SEPI lines we have $\Delta\nu_L = 2 \ln 2/\pi t_p = 0.44/t_p$. Choosing $t_p \gtrsim 1.4 T_2$ one achieves a higher resolution in the SEPI spectra.

As pointed out above, the electric field E_{L2} of the third pulse gives a coherent Stokes-shifted signal of the form

$$S^{\mathrm{coh}}(t, t_D) \propto \int \mathrm{d}\tilde{x} \sum_i E_{L2}(\tilde{x}, \tilde{t} - t_D)\, Q_i^*(\tilde{x}, t)\,, \tag{1}$$

where S^{coh} is written for the moving frame of the Stokes pulse with $\tilde{x} = x$ and $\tilde{t} = t - x\mu_{S2}/c$. We recall that phase matching $k_{S2i} = k_{L2} - k_i$ is necessary for a strongly scattered Stokes wave. In our geometry (forward direction) phase matching of the different vibrational modes is readily established. Fourier transformation of eq. (1) yields the coherent spectrum

$$I(\omega) \propto \left| \int_{-\infty}^{\infty} \mathrm{d}t\, \exp(\mathrm{i}\omega t)\, S^{\mathrm{coh}}(t, t_D) \right|^2 . \tag{2}$$

For a gaussian shape of the monitoring pulse, disregarding the overlap of the scattered spectra, we may integrate eq. (2) for long delay times t_D:

$$I(\omega) \propto \sum_i I_{0i} \exp(-2t_D/T_{2i}) \times \exp\{(\omega - \omega_{S2i})^2 \, [\pi\Delta\nu_L/(\ln 2)^{1/2}]^{-2}\}. \quad (3)$$

I_{0i} accounts for the degree of excitation of the ith component at time zero. According to eq. (3) the SEPI spectrum consists of a sum of bands of gaussian shape and with the halfwidth $\Delta\nu_L = 0.44/t_p$ determined by the interrogating pulse. The peak position of the different bands provides the frequencies of the vibrational modes $\omega_i = \omega_{L2} - \omega_{S2i}$. Vibrational modes with shorter dephasing times or with smaller excitation have smaller peaks in the scattered spectrum.

4. An example: cyclohexane between 2850 and 2940 cm^{-1}

As an example of the practicability of the SEPI technique we present Raman data of cyclohexane in the small frequency range between 2850 and 2940 cm^{-1}. In fig. 2b the polarized spontaneous Raman spectrum is depicted. This spectrum was taken with an Ar$^+$ laser and a Raman spectrometer with a resolution better than 1 cm^{-1}. The three strong Raman bands correspond to CH-stretching modes and the diffuse spectrum between 2860 and 2920 cm^{-1} is considered to be due to overlapping overtones and combination modes which are enhanced by Fermi resonance with the fundamentals [6,7].

In fig. 2c we show three SEPI spectra on an expanded scale (factor 3.7). Each spectrum was obtained with a single laser shot. On the rhs we present the sharp SEPI band corresponding to the CH-stretching mode at 2923 cm^{-1}. The small linewidth of 2.3 cm^{-1} allows us to determine accurately the peak position at 2922.0 ± 0.7 cm^{-1}. We note that the SEPI band is considerably smaller than the corresponding band in the spontaneous Raman spectrum of fig. 2b, the latter being asymmetric on account of other weaker Raman transitions. The Raman transition at 2923 cm^{-1} was excited using ethylene glycol, $(CH_2OH)_2$, in the generator cell of fig. 1.

The SEPI spectrum of fig. 2c, middle, shows four Raman transitions. Lines as close as 2.5 cm^{-1} are clearly resolved. The four transitions are hidden under the wing of the strong Raman band at 2923 cm^{-1}; they cannot be detected in the conventional Raman spectrum of fig. 2b. The SEPI spectrum is obtained using an exciting pulse ν_2 with a frequency band extending from 2900 to 2920 cm^{-1} (dimethyl sulfide, C_2H_6S, in the generator).

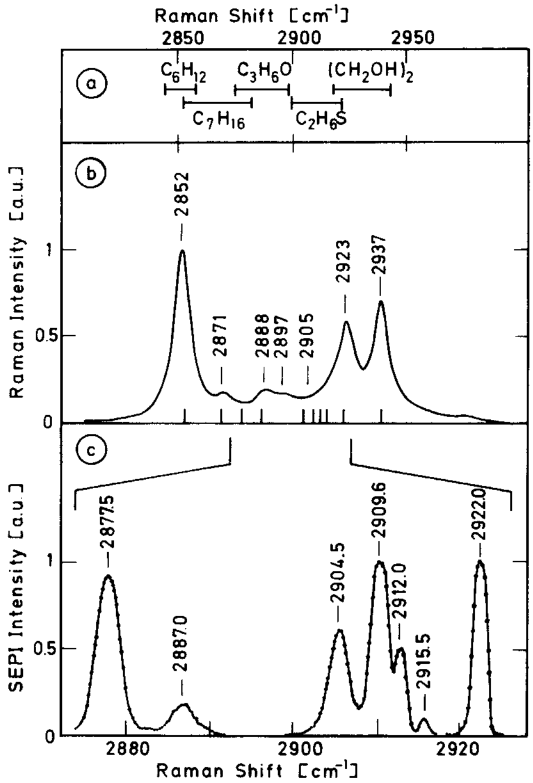

Fig. 2. Experimental results of SEPI spectroscopy of C_6H_{12}. (a) Frequency ranges of the various generator liquids used in the experiment. (b) Polarized spontaneous Raman spectrum of C_6H_{12} recorded with a resolution of 1 cm^{-1}. The frequency positions of the resonances found in SEPI spectra are marked by 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 in (c) is 3.7 times larger than that in (b).)

In fig. 2c, lhs, we depict a SEPI spectrum obtained after excitation by a ν_2 pulse with a spectral bandwidth extending from 2875 to 2890 cm^{-1} (propylene oxide, C_3H_6O). We find two distinct Raman bands at 2877.5 and 2887 cm^{-1}. The band at 2877.5 cm^{-1} has not previously been reported. It is buried in the diffuse part of the conventional Raman spectrum (see fig. 2b).

Table 1
Frequency positions of vibrational modes in liquid C_6H_{12} in the frequency range 2850 to 2940 cm^{-1}

SEPI spectra	Spontaneous Raman scattering [6,7]
2852.2 ± 0.7	2852, 2853
(2874)	2871
2877.5 ± 1.5	–
2887.0 ± 0.8	2888
–	2897
2904.5 ± 1.0	2905
2909.6 ± 0.7	–
2912.0 ± 0.8	–
2915.5 ± 1.5	–
2922.0 ± 0.7	2923
2937.5 ± 0.7	2936, 2938

In table 1 the peak positions of the SEPI lines and of the Raman bands reported in the literature are listed for comparison. Four new Raman lines are found in the SEPI spectra within the small frequency range. In addition, the accuracy of the peak positions is considerably better in the SEPI measurements.

At the bottom of fig. 2b the frequency positions of the Raman bands found in our SEPI spectra are marked by vertical lines. One readily sees the new Raman lines which cannot be inferred from the spontaneous Raman spectrum.

Some remarks should be made on the Raman bands at 2871 and 2897 cm^{-1} which are faintly seen in fig. 2b and which are called "broad" in the literature. These Raman transitions are not observed in the SEPI spectra with delay times of ≈20 ps. The band at 2871 cm^{-1} was found with a shorter delay time of the third pulse and seen to be quite broad. The Raman transition at 2897 cm^{-1} was not effectively excited. We conclude from our observations that the dephasing times of the two Raman lines are very short or that the lines are (partially) inhomogeneously broadened. The observation of different dephasing times of closely spaced Raman lines is interesting in itself and requires further study.

A final assignment of the eight weak Raman lines between 2870 and 2920 cm^{-1} has not yet been made. Inspection of the lower fundamental modes suggest overtones and combination modes in this frequency range. Of special interest is the new Raman line at 2912 cm^{-1} which coincides precisely with an infrared active mode of the molecule [8]. It appears that we observe here a Raman-forbidden mode.

5. Additional observations and comments

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. We have tested this notion, exciting our sample with narrow or with broad pulses of similar central frequency ν_2. This experiment is readily performed using different media in the generator cell. The advantage of a broad frequency spectrum of the incident pulse is to provide initial conditions for several Raman transitions in congested frequency regions. One can observe several Raman lines with one shot (see fig. 2c, middle). (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. For this reason, the delay time of the third probing pulse has to be sufficiently large. One roughly estimates delay times of $t_D = 20–25$ ps for dephasing times $T_{2i} \approx 1$ ps and gaussian pulses of 8 ps duration. The SEPI spectra are observed with good accuracy, approximately five orders of magnitude below the peak value at $t_D = 0$. (iii) The maxima of the SEPI spectra are not proportional to the Raman scattering cross section, since the initial conditions of the exciting pulses and the T_{2i} times are important parameters for the observed magnitude of the generated signal [eq. (3)]. 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. Interrogating pulses with a chirped frequency spectrum give unwanted shifts of the SEPI spectra and thus should be avoided. (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 [4,9,10]. (vi) A simultaneous measurement of the coherent Stokes and anti-Stokes SEPI spectra allows us to eliminate the effect of a chirped probing pulse. In this way the absolute frequency position is obtained with high accuracy [4].

6. Summary

The data presented in the preceding sections give convincing evidence of the potentiality of the short excitation and prolonged interrogation spectroscopy; new Raman lines are readily observed and energy states are determined with improved accuracy. We expect this new type of spectroscopy to become a valuable tool for the rapid acquisition of Raman data not available from other known techniques.

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