New investigations of polyatomic molecules in the liquid state using picosecond light pulses

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A description is given of a new method for investigating vibrational excitations of molecules in liquids: this method involves a preliminary brief excitation of a molecule by two picosecond pulses, differing in frequency by an amount which is in resonance with natural vibrations of the molecule, followed by a subsequent prolonged investigation of free relaxation of the excited system. The results are reported of an investigation of this kind made on C_6H_{12} in the range 2875–2925 cm^{-1}. Lines not resolved in the usual spontaneous Raman spectrum were observed. The position of the well-known 2923 cm^{-1} line was determined more accurately.

For many years the band contours of Raman transitions have been the main source of dynamic information on polyatomic molecules. However, in most cases it is difficult to separate the Raman band of interest from the background made up of other neighboring or weak overlapping Raman transitions. In the case of polyatomic molecules there are many overtones and combination modes which may contribute—possibly enhanced by a Fermi resonance—to the observed scattered-light intensity.

When a band contour is determined accurately, difficulties are encountered in the interpretation of the physical origin of the Raman band width. In general, there are several line-broadening mechanisms which may or may not contribute to the observed Raman band. These include collision-induced dephasing, energy relaxation of excited vibrational states, possible isotopic multiplicity of a transition, and finally inhomogeneous broadening due to changes in the molecular environment.

Recently we were able to determine directly the population lifetime T_1 and the dephasing time T_2 of various vibrational modes in the time domain without recourse to the width of the vibrational transition lines.[1-5] In the case of polyatomic molecules in the liquid state at 300 °K both time constants T_1 and T_2 are very short, frequently of the order of picoseconds. Consequently, we had to design experimental systems to enable us to measure vibrational time constants on the time scale of 10^{-12} sec. In the present paper we shall review experimental techniques and report new results to illustrate the state of our knowledge of the population lifetime T_1. In addition we shall describe a novel coherent Raman technique which can be used to detect new Raman lines in congested spectral regions.

POPULATION LIFETIME T_1

The population lifetime of a specific vibrational state is measured as follows. The first ultrashort infrared pulse, turned to the resonance frequency of the investigated transition, excites molecules by direct infrared absorption, whereas the second visible pulse follows after a variable delay time and it monitors the instantaneous population of the excited molecules. A spontaneous anti-Stokes Raman signal is used as a direct measure of the excess population. This technique has the great advantage of providing very direct information on the populated vibrational mode. Observation of various anti-Stokes frequencies tells us accurately which vibrational mode is populated at a certain time. In this way we are able to observe the time dependence of the primary excitation and to follow the vibrational energy through different decay relaxation) channels.

However, this technique for the determination of T_1 has a major shortcoming. The Raman scattering cross sections are notoriously very small and the population densities achieved after a short excitation pulse do not exceed 1%. Consequently, the number of scattered photons is very small, approximately from 10^2 to 10^3 per pulse, which makes the data acquisition a nontrivial task.[4]

EXPERIMENTAL SYSTEM FOR MEASURING T_1

Figure 1 shows schematically a more advanced experimental system for the determination of T_1. Two pulses differing considerably in frequency were generated. A tunable infrared pulse of frequency ν_1 is generated by a three-photon process in three lithium niobate crystals.[6] Typical intensities of infrared pulses were 10^{16} photons per pulse and the spectral band width was $\Delta \bar{\nu}_{IR} \approx 20$ cm^{-1}, and the beam divergence was
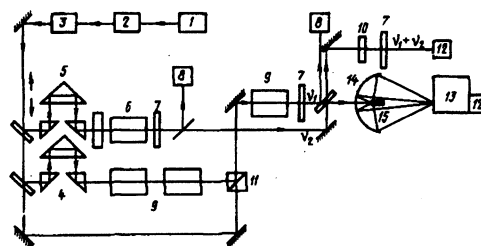

FIG. 1. Schematic diagram of the system used to measure the population lifetime T_1 of vibrational modes: 1) Q-switched laser; 2) switch; 3) amplifier; 4), 5) fixed and controlled optical delay lines; 6) KDP crystals; 7) optical filters; 8) photodiodes; 9) lithium niobate crystal; 10) lithium niobate plate; 11) polarizer; 12) photomultiplier; 13) spectrograph; 14) ellipsoidal mirror; 15) investigated sample.

~1 μrad. A monitoring green pulse ($\tilde{\nu}_2 = 18\,990$ cm^{-1}) was generated in the form of the second harmonic frequency in a nonlinear KDP crystal. Both pulses were focused (after the selected delay time) in a small sample located at the focus of an ellipsoidal mirror. Approximately 50% of the anti-Stokes scattered photons were collected by this mirror and imaged at the entrance slit of a spectrometer connected to a photomultiplier. After different delays, both pulses were mixed in a thin lithium niobate crystal (10 in Fig. 1), generating the sum frequency. In this way we obtained the cross-correlation function for each experimental run. The peak of the cross-correlation function corresponded to zero point on our time scale (where the maxima of both pulses overlapped) and the width of the cross-correlation function yielded valuable information on the time resolution in each experiment.

RECENT RESULTS AND DISCUSSION OF T_1 DATA

We investigated numerous molecules and found widely varying values of the population lifetimes between 1 psec (corresponding to the time resolution of our system) and 200 psec in the case of polyatomic molecules at room temperature.[1,2,4] Special attention was paid to the stretching modes of the CH groups in the frequency range 3000 ± 100 cm^{-1}, where direct pumping by infrared pulses was particularly effective.

At the beginning of our investigations we found the large spread in the T_1 values quite puzzling. The lifetimes T_1 appeared to be very sensitive to the specific level structure of the individual molecule. In the past few years we made a considerable progress in our understanding of the physical phenomena determining the population lifetime of polyatomic molecules. One should distinguish two processes.

The first process represents a very rapid exchange of the vibrational energy between similar fundamental vibrations with similar energies. For example, we have experimental evidence that collision-induced interactions lead to a rapid energy exchange (faster than 1 psec) between the symmetric and asymmetric stretching modes of the CH$_2$ group. Consequently, excitation with pulses of 5 psec duration populates both vibrational levels. Indeed, a very fast energy exchange (faster than 1 psec) occurs between the infrared and Raman-active modes within the CH fundamentals. This observation has consequences for the decay (relaxation) process which starts—after the pump pulses left the medium—from a reservoir of two or more energy states.

In the second process the vibrational energy is transferred from the CH stretching modes (~3000 cm^{-1}) via overtones and combination modes to lower energy states. An intramolecular anharmonic coupling (a Fermi resonance) between neighboring energy states is of major importance in this respect. The degree of a Fermi resonance in a certain frequency range manifests itself in the infrared and Raman spectra. Overtones and higher-order combination modes "borrow" intensity from the CH stretching modes. We shall use the intensity ratio R between the final and initial

states, taken from an infrared or Raman spectrum, as a measure of the Fermi resonance mixing. Recently, Fendt, Fischer, and Kaiser[1] derived a formula for estimating the lifetime T_1 of a vibrational state:

$$T_1 \sim N(1-R)^2 R^{-1} \exp(\omega/\Omega)^2 \, {}^3T_2(f),$$

where N corresponds to the number of initially excited states and $T_2(f)$ is the dephasing time of the final state. This time can be estimated from the Raman line width $\Delta\nu$ as $T_2(f) = (2\pi c\Delta\nu)^{-1}$, where $T_2(f)$ is equal to $T_2/2$ measured in coherent Raman experiments.[3]

The frequency ω represents the energy difference between the initial and final states, whereas the frequency Ω has a value close to 100 cm^{-1}. In some cases a complex band structure prevents determination of $T_2(f)$. Moreover, the above equation for T_1 breaks down for a very strong vibrational coupling when the Fermi resonance interaction becomes so strong that the energy transfer process is very fast, i.e., it occurs within the excitation pulse duration.

As an example, we shall report the data on two molecules: CH$_2$ = CCl$_2$ and trans-CHCl = CHCl, the infrared absorption and Raman spectra of which are shown in Fig. 2 (Ref. 4). The two molecules have very similar structures: they differ only by a change in the positions of two atoms. Figure 3a shows the symmetric (ν_1) and asymmetric (ν_7) stretching vibrations of the CH$_2$ group in CH$_2$ = CCl$_2$ in a strong Fermi resonance with combination modes. In particular, there is a strong Fermi resonance between the modes ν_1 and $\nu_2 + \nu_3$, both of the A_1 symmetry, and also between ν_7 and $\nu_2 + \nu_6 + \nu_{11}$, both of which are of the B_1 symmetry.[4] This observation suggests that we have to consider two decay channels for the relaxation of the stretching modes of CH$_2$. In the case of the $\nu_1 \rightarrow \nu_2 + \nu_3$ process we can estimate the intensity ratio $R = 0.2 \pm 0.05$ and calculate $T_2(f) = 0.3$ psec employing the Raman line width $\Delta\nu = 17$ cm^{-1}. For $N = 2$ (two CH$_2$ modes) and $\omega = 40$ cm^{-1}, we find from Eq. (1) that $T_1 = 7.8 \pm 3$ psec.

In the case of the second decay channel $\nu_7 \rightarrow \nu_2 + \nu_6 + \nu_{11}$, the parameters are $R = 0.6 \pm 0.1$, $T_2(f) = 0.3$ psec, $N = 2$, and $\omega = 45$ cm^{-1}, which gives $T_1 = 4.5 \pm 1$ psec. Adding the two decay rates we obtain an estimate of the
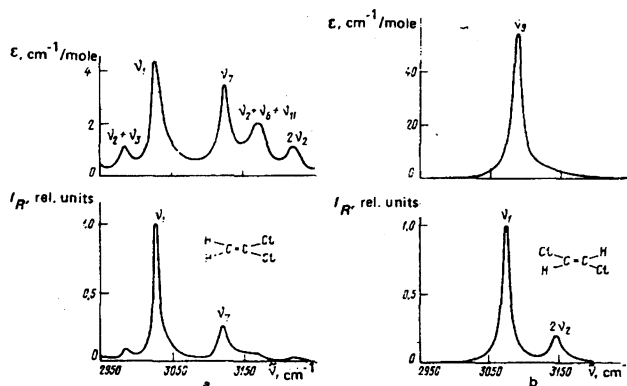

FIG. 2. Infrared and Raman spectra of CH$_2$ = CCl$_2$ (a) and CHCl = CHCl (b) in the spectral interval 2950–3250 cm^{-1} (here, ε represents infrared absorption).
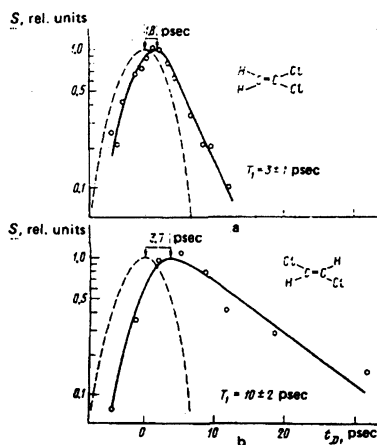
FIG. 3. Anti-Stokes scattering signal S plotted as a function of the delay time of a probe pulse t_D in solutions of $CH_2 = CCl_2$ (a) and trans-$CHCl = CHCl$ (b) at a concentration 0.35 molar fractions: a) $\tilde{\nu}_1 = 3036$ cm^{-1}, $\tilde{\nu}_2 = 3036$ cm^{-1}; b) $\tilde{\nu}_1 = 3084$ cm^{-1}, $\tilde{\nu}_2 = 3073$ cm^{-1}. The dashed curves represent cross-correlation functions of the exciting (infrared) and interrogating (green) pulses.

relaxation time for the two CH_2 stretching modes: $T_1 = 2.9 \pm 0.6$ psec.

Figure 3a gives the results of the direct experimental determination of the time constant T_1 for the stretching modes of CH_2. The ν_1 mode at 3036 cm^{-1} is resonantly excited by an infrared pulse and the anti-Stokes scattering of the same ν_1 mode is observed. The scattered Raman signal rises to a slightly delayed maximum during the excitation process and decays with a relaxation time $T_1 = 3 \pm 1$ psec. This experimental value is in excellent agreement with the calculated time constant T_1 discussed in the preceding paragraph. The dashed curves in Fig. 3 represent the cross-correlation. As pointed out above, they determine the zero point on the time axis and give a good indication of the time resolution of the apparatus.

Figure 2b shows the infrared-active stretching mode ν_9 and the Raman-active symmetric mode ν_1 of trans-$CHCl = CHCl$. Here we find a much weaker Fermi resonance. The Raman spectrum of Fig. 2b suggests some anharmonic coupling between ν_1 and $2\nu_2$, both of the A_g symmetry. Assuming that $R = 0.15 \pm 0.02$, $T_2(f) = 0.3$ psec, $N = 2$, and $\omega = 80$ cm^{-1}, we find that $T_1 = 13$ psec.

Figure 3b gives the time dependence of the stretching modes of CH in trans-$CHCl = CHCl$. This molecule is excited via the ν_9 mode at 3084 cm^{-1} and the population of the ν_1 mode at 3073 cm^{-1} is monitored by anti-Stokes Raman scattering. The rapid rise of the Raman signal, i.e., the fast filling of the ν_1 mode, provides clear evidence of fast energy exchange between the two CH fundamentals ν_1 and ν_9. The slow decay of the signal shows that the lifetime of two stretching modes of CH is long: $T_1 = 10 \pm 2$ psec. This result is in good agreement with the value estimated above. A weak intramolecular coupling is responsible for the longer vibrational lifetime.

DEPHASING TIME T_2

In our investigations a specific vibrational mode was first coherently excited via the stimulated Raman effect and the time dependence of the vibrational excitation was monitored subsequently by a delayed and properly phase-matched probe pulse. The situation was straightforward for homogeneously broadened Raman transitions,[5] when the probe signal decayed exponentially with time, providing directly the value of the dephasing time T_2. In a number of cases it was possible to show that the dephasing time accounted fully for the band width of the Raman transition $\Delta\tilde{\nu}_R$ in accordance with the relationship $T_2 = 1/\pi c \Delta\tilde{\nu}_R$.

More recently, various theoretical papers have appeared to relate the collision-induced dephasing time to molecular parameters.[7] In some cases the agreement between the theory and experiment is satisfactory.

NEW RAMAN SPECTROSCOPY UTILIZING SHORT COHERENT EXCITATION AND SUBSEQUENT PROLONGED INTERROGATION

We shall describe here a new spectroscopic technique[8,9] which provides information on homogeneously broadened transitions. New Raman lines can be detected in congested spectral regions and peak positions of Raman lines in liquids can be measured with unprecedented accuracy.

The idea underlying this new Raman technique is as follows. During a short transient excitation process the molecules in a liquid are driven by two light pulses separated by a frequency difference ν_D. Raman transitions at and close to ν_D become excited and they have coherent amplitudes Q_j. This coherent excitation persists even when the two pump pulses have left the liquid sample. The molecules regain their resonance frequencies ν_j and the amplitude Q_j decay with the characteristic dephasing time T_{2j}. During the free relaxation process a third delayed long-duration probe pulse interacts with the coherently vibrating molecules. It generates coherently scattered Raman-shifted light carrying valuable information on the molecules. Only the molecules vibrating in phase during the probing process contribute to the coherent signal. The molecules which have suffered dephasing collisions vibrate out of step and are not observed. In the case of a suitable shape (for example, Gaussian) of the long-duration interrogating pulse the measuring time may be increased and the spectral resolution improved. This technique is based on short excitation and prolonged interrogation (SEPI) of molecular states.[5,8,9]

EXPERIMENTAL SYSTEM FOR SHORT EXCITATION AND PROLONGED INTERROGATION SPECTROSCOPY

The short dephasing times of vibrational modes in molecular liquids require picosecond pulses in order to measure SEPI spectra. It is convenient to use exciting pulses with a band width ~10 cm^{-1} tuned in steps over a wider frequency range. For each excitation band the coherent spectrum should be recorded by a spectrometer or spectrograph with a sufficient resolution. Fig-
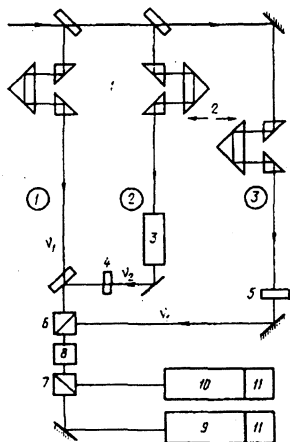
FIG. 4. Schematic diagram of a system used to study SEPI spectra of liquids: 1), 2) fixed and controlled optical delay lines; 3) Raman generator; 4) optical filter; 5) λ/2 plate; 6), 7) crossed polarizers; 8) investigated sample; 9), 10) spectrographs; 11) optical spectrum analyzer.
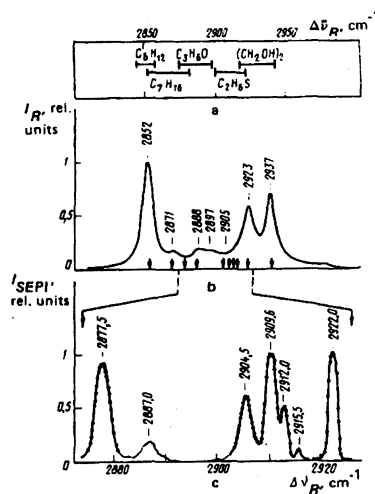

FIG. 5. Spectral intervals of various liquids used in the Raman generator (a), polarization spectra of the Raman scattering in C_6H_{12} recorded with a resolution of 1 cm⁻¹ (b) and three SEPI spectra obtained using three different liquids in the Raman generator (c). The arrows identify the positions of resonance lines observed in the SEPI spectrum.

ure 4 shows schematically our apparatus. A single frequency-doubled pulse from a mode-locked Nd glass laser (shown in the top left-hand corner of Fig. 4) was used[10]; the duration of this pulse was 8 psec and its frequency was 18 990 cm⁻¹. Two consecutive beam splitters were used to divide the pulse into three parts. The pulse in the first beam passed through a polarizer 6 and a sample, but was then blocked by a crossed polarizer 7. The second beam altered the frequency to ν_2 in a generator utilizing stimulated Raman scattering. A change in the working medium in the Raman generator readily produced pulses of different frequencies ν_2. These pulses were blocked by the polarizer 7 and were spectrally monitored by a spectrograph 10. In view of the transient nature of the generation process, the pulses of frequency ν_2 were shorter by a factor of about three than the incident pulses at the frequency ν_1 (Ref. 11). The two pulses in the first and second beams reached the sample simultaneously and excited coherently molecular vibrations because of transient stimulated Raman scattering at the difference frequency $\nu_D = \nu_1 - \nu_2$. In the third optical path a delayed pulse with the polarization perpendicular to that of the pulses in the first and second beams was generated. This third pulse interacted with the coherently excited molecules in the sample producing a Raman-shifted signal pulse. Stokes scattering ensured that the three pulses traveled collinearly through the sample. In the case of anti-Stokes scattering, the probe pulse crossed the beam of the excited pulses at the phase-matching angle. The spectrum of the coherently scattered light was scattered using a two-meter spectrograph 9 and a cooled optical spectrum analyzer 11. The system had a resolution of 0.2 cm⁻¹ per channel and an absolute accuracy of the frequency scale of 0.4 cm⁻¹.

EXPERIMENTAL RESULTS ON LIQUID CYCLOHEXANE

We carried out SEPI measurements on a number of organic and inorganic liquids. We shall give here the

results on liquid CH_6H_{12} with broad and overlapping lines between 2850 and 2440 cm⁻¹ in the usual spontaneous Raman spectrum. Figure 5b shows the polarized (spontaneous Raman) spectrum. This spectrum was recorded using an argon laser and a Raman spectrometer with a resolution better than 1 cm⁻¹. The three strong Raman bands observed in the spectrum were due to the CH stretching modes and the diffuse spectrum between 2860 and 2930 cm⁻¹ was attributed to overlapping overtones and combination modes enhanced by a Fermi resonance with the fundamentals.[12,13]

Figure 5c shows three SEPI spectra on an expanded scale (by a factor of 3.7). Each spectrum was obtained using a single laser shot. On the right we plotted a sharp SEPI band corresponding to the CH stretching mode at 2923 cm⁻¹. The small line width of 2.3 cm⁻¹ enabled us to determine accurately the peak position as 2922.0 ± 0.7 cm⁻¹. The SEPI band was considerably narrower than the corresponding band in the spontaneous Raman spectrum of Fig. 5b. Moreover, the latter was asymmetric because of other weaker Raman transitions. The Raman transition at 2923 cm⁻¹ was excited using ethylene glycol $(CH_2OH)_2$ in the Raman generator cell (Fig. 4).

The SEPI spectrum of Fig. 5c located to the left of the 2923 cm⁻¹ line consisted of four Raman transitions. We resolved clearly the lines separated by just 2.5 cm⁻¹. The four transitions were hidden under the wing of the strong Raman band at 2923 cm⁻¹ and they could not be detected in the conventional Raman spectrum of Fig. 5b. The SEPI spectrum was obtained using an exciting pulse of frequency ν_2 in the band 2900–2920 cm⁻¹ (dimethyl sulfide C_2H_6S was used in the Raman generator).

On the left hand side of Fig. 5c we plotted a SEPI spectrum obtained after excitation by a ν_2 pulse with a

spectral band width 2875–2890 cm^{-1} (propylene oxide C$_2$H$_6$O was used in the Raman generator). We found two distinct Raman bands at 2877.5 and 2887 cm^{-1}, the former of which had not been detected earlier, because it was buried in the diffuse part of the conventional Raman spectrum (Fig. 5b).

The final identification of the new Raman lines observed in the interval 2870–2920 cm^{-1} has not yet been made. Inspection of the lower fundamental modes suggests 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. It appears that this is a forbidden Raman mode.

ADDITIONAL OBSERVATIONS AND COMMENTS ON SHORT EXCITATION AND PROLONGED INTERROGATION SPECTRA

The following points are important in the application of the SEPI technique.

The frequency positions of the observed Raman lines are independent of the excitation conditions, since we are observing freely relaxing molecules. We have tested this notion by exciting a sample with narrow- or broad-band pulses of similar central frequency ν_2. The advantage of a broad-band frequency spectrum of the incident pulse is the provision of initial conditions for several Raman transitions in congested spectral regions. One can then observe several Raman lines employing a single laser short (middle part of Fig. 5c).

The exciting and interrogating pulses in SEPI experiments should not overlap on the time scale in order to avoid the generation of a coherent signal via a nonresonant four-photon parameteric process. For this reason the delay time of the third probe pulse should be sufficiently large. One can roughly estimate the delay times of $t_D = 20$–25 psec for dephasing times $T_{2j} = 1$ psec and Gaussian pulses of 8 psec duration. The SEPI spectra are observed with a good accuracy, approximately five orders of magnitude below the peak value at $t_D = 0$.

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 dephasing times T_{2j} are important in the observed magnitude of the generated signal. The SEPI spectra obtained after different delay times allow us to estimate the values of T_{2j}.

The frequency precision of the generated Stokes spectrum depends on the frequency stability of the integrat-

ing pulses. For the highest accuracy the frequency ν_1 should be determined simultaneously with the SEPI spectrum. If an interrogating pulse has a chirped frequency spectrum, unwanted shifts appear in the SEPI spectra and such pulses should be avoided.

The scattering process may also occur on the anti-Stokes side of the spectrum. The disturbing interference found in stationary CARS spectroscopy does not occur in the delayed probing used in the SEPI spectroscopy.[9,14]

Finally, simultaneous determination of the coherent Stokes and anti-Stokes SEPI spectra allows us to eliminate the effects of a chirped probe pulse. In this way the absolute frequency position is determined with a high accuracy.[9]

CONCLUDING REMARKS

The data presented in this article demonstrate convincingly the usefulness of coherent and incoherent picosecond measurements. We can obtain molecular information and that cannot be found by other existing spectroscopic techniques.

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