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Applications of Picosecond and Sub-
Picosecond Spectroscopy

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Vibrational relaxation processes have received increasing interest in recent years. With ultrashort light pulses and novel experimental techniques we are in the position to study vibrational dynamics in the electronic ground state of simple liquids on the subpicosecond and picosecond time scale. In this brief summary two topics will be discussed.

Vibrational Population Lifetimes of ($v=1$) and ($v=2$) levels

Ultrafast population decay and energy transfer have been recently observed in several systems (1-4). These processes are particularly interesting since they are not accessible with standard spectroscopic techniques. More systematic studies for a larger variety of molecular systems are highly desirable for an improved understanding of the physical mechanism. We have devised a versatile picosecond Raman spectrometer for the measurement of population lifetimes in liquids, which achieves a significant reduction of measuring time and/or improvement of experimental accuracy by an increased pulse repetition rate (5). The system applies tunable excitation pulses of 10 ps and 200 μ J in the infrared around 3 μ m. The properly tuned pump pulses are focused into the sample and promote the molecules to an upper vibrational state via resonant infrared absorption. The excited molecules are subsequently interrogated by green probing pulses. Spontaneous anti-Stokes scattering is observed as a direct measure of the instantaneous excess population of the excited vibrational level.

We have investigated CH_2 -modes of several methylene halides and of $(\text{CH}_2\text{Cl})_2$ in the neat liquid and dissolved in CCl_4 (5). The first excited state of the symmetric stretching mode ν_1 was excited by the resonantly tuned IR pulse. Examples for the time-resolved data are presented in Fig. 1. The measured time-integrated anti-Stokes scattering signal $S(t_D)$ of the probe pulse is plotted on a semi-logarithmic scale versus delay time t_D between probe and excitation pulses (full and open points). The individual experimental points indicate the accumulated information of 200

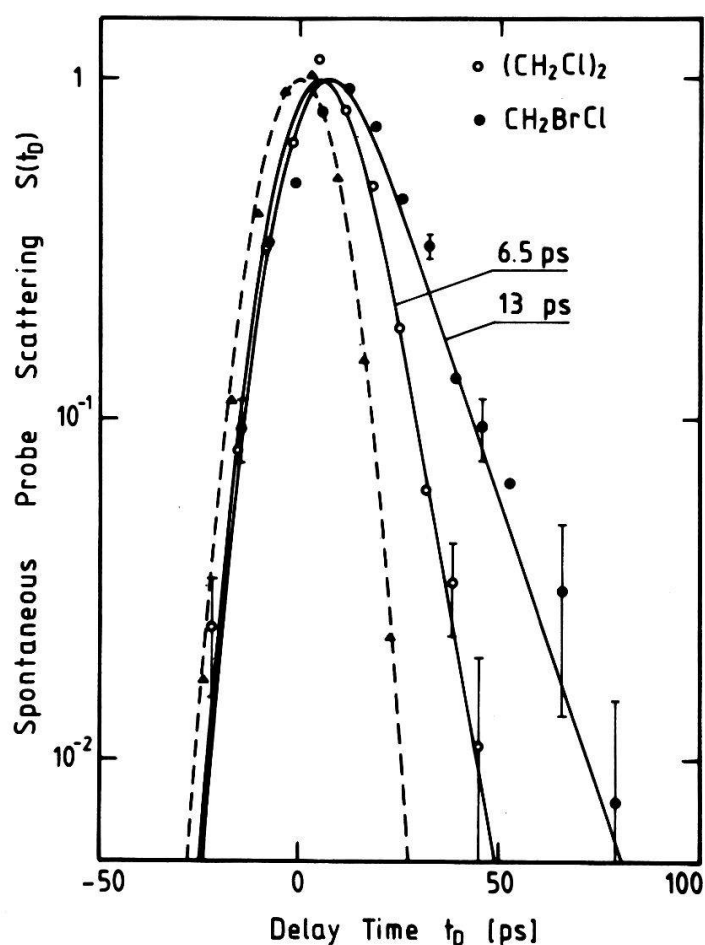


Figure 1. Spontaneous anti-Stokes scattering signal $S(t_D)$ of the probe pulse versus delay time t_D for the symmetric CH_2 -stretching modes of $(\text{CH}_2\text{Cl})_2$ (o) and CH_2BrCl (●); broken line and full triangles represent the instrumental response of the $(\text{CH}_2\text{Cl})_2$ measurement.

to 600 laser shots and extend over a factor of ~ 100 . The population lifetime T_1 is directly obtained from the exponential decay of the signal points in Fig. 1 for larger values of t_D . The full triangles in the figure show results of a simultaneous reference experiment measuring the cross correlation function between excitation and probing pulses, which represents the instrumental response of the experimental system.

The curves are calculated assuming Gaussian shape of the light pulses and using the population lifetime T_1 as fitting parameter. It is interesting to see that the delay of the signal maxima and the asymptotic decay are fully accounted for by the theoretical curves. Results on T_1 are listed in Table I, which indicates values of 6.5 to 45 ps for the investigated CH-stretching modes. Data on $(\text{CH}_2\text{ClCH}_2)_2\text{O}$ are included to demonstrate the time resolution of the measuring system.

Table I. Measured population lifetimes T_1 of CH-stretching modes

	concentration vol %	$\tilde{\nu} \text{ cm}^{-1} \text{ }$	$T_1 \text{ ps }$
CH_2Br_2	100	2987	7 ± 1
	30	2987	7 ± 1
CH_2Cl_2	100	2989	12 ± 2
	10	2989	12 ± 2
CH_2I_2	50	2967	45 ± 5
CH_2ClBr	30	2987	13 ± 2
CH_2ClI	30	2979	14 ± 2
$(\text{CH}_2\text{Cl})_2$	10	2950	6.5 ± 1
CHBr_3	100	3020	40 ± 4
CHBr_3	100	5920	5 ± 1
$(\text{CH}_2\text{ClCH}_2)_2\text{O}$	5	~ 2964	2 ± 2

The population lifetimes are explained by vibrational energy transfer via anharmonic coupling to neighbouring combination bands and overtones. Numerical estimates have been performed considering Fermi resonance with the adjacent overtone of the CH_2 -bending mode (4) yielding only fair agreement. It is concluded

that higher order combination bands in the immediate neighbourhood of the symmetric stretching mode give a notable contribution to the observed population decay.

In the past the investigations have been restricted to the excitation of $v=1$ states. The improved measuring sensitivity of our experimental system allows for the first time to study higher excited vibrational levels after direct population via overtone absorption (6). Monitoring the transient population of lower-lying states it is also possible to obtain information on decay channels. Decay routes have been previously studied in a few cases only, (2,7).

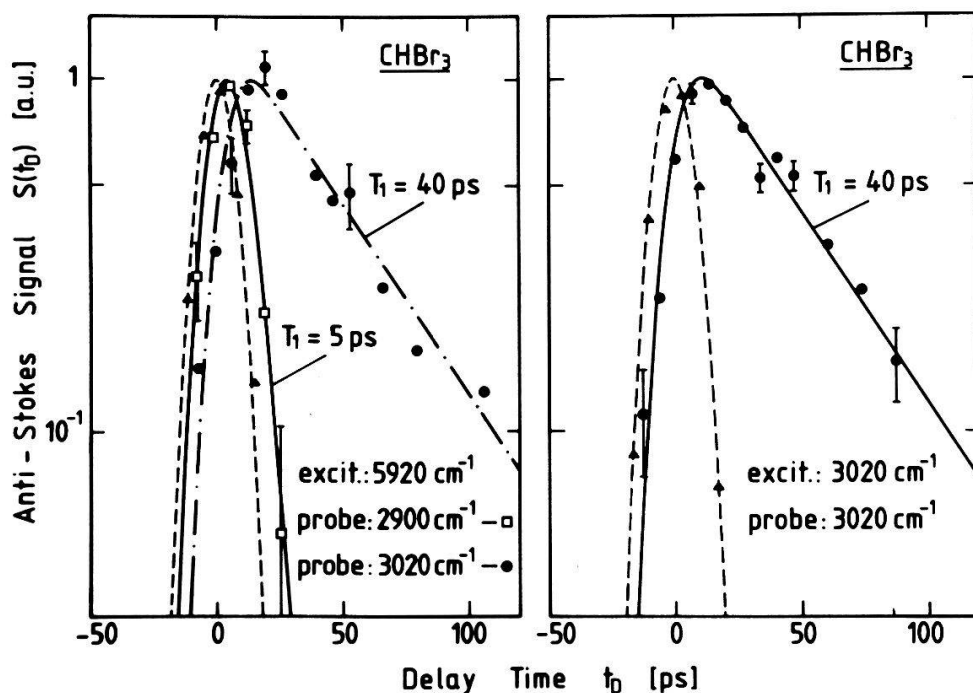


Figure 2. Spontaneous anti-Stokes probe scattering $S(t_D)$ of the CH-stretching mode of neat CHBr_3 :

- a) $v=2$ state (\square ; solid line) populated by overtone absorption at 5920 cm^{-1} and $v=1$ state (\bullet , dash-dotted line) populated by energy transfer from ($v=2$);
 - b) directly populated $v=1$ state (\bullet ; solid line);
- instrumental response curves (\blacktriangle ; broken lines).

An example for overtone excitation and direct observation of vibrational-vibrational energy transfer is shown in Fig. 2. The first and second excited levels of the CH-stretching mode ν_1 of neat CHBr_3 is investigated. In Fig. 2a the infrared excitation pulse is tuned to the $2\nu_1$ overtone of the CH-vibration at 5920 cm^{-1} . The transient population of the $v=2$ state is directly observed measuring the spontaneous Raman scattering of the probe pulse with an anti-Stokes frequency shift of 2900 cm^{-1} , the transition frequency from $v=2$ to $v=1$. The scattering signal is plotted in the Fig. (open squares, full line) versus delay time. A population lifetime $T_1(v=2) = 5 \pm 1\text{ ps}$ is obtained from the decaying part of the signal curve for the second excited level.

Fig. 2a also presents direct evidence for efficient energy transfer from $v=2$ to the $v=1$ state. Scattering signals with anti-Stokes shift of $\nu_1 = 3020\text{ cm}^{-1}$ (full points) are observed which represent a transient excess population of the first excited level. The delayed maximum of the calculated signal curve (dash-dotted line) reflects the population of the $v=1$ state during the relaxation of the upper level. The decay of the full points for larger t_D in Fig. 2a yields the population lifetime $T_1 = 40 \pm 4\text{ ps}$ for $v=1$. This result is supported by the data of Fig. 2b. Here the first excited level was directly populated by an excitation pulse tuned to 3020 cm^{-1} and monitored by the probing process. The same time constant is found. Comparison of the magnitude of the probe scattering signals in Fig. 2a suggests a high efficiency of the energy transfer process $\geq 50\%$.

Nonexponential Dephasing in the Subpicosecond Time Domain

In the past several investigations of the vibrational dephasing time T_2 in liquids have been performed (8). In these studies exponential decay of the coherent vibrational excitation has been observed. No direct information has been available on the short time behaviour, $t \leq 1\text{ ps}$. Similarly, for theoretical work on stimulated Raman scattering purely exponential time behaviour was assumed. It is, however, known from theory of relaxa-

tion processes that this approximation does not hold for very short times which compare with the time scale of the dephasing mechanism (9). We have generalized the theory of transient stimulated Raman scattering to include non-exponential dephasing (10). Our approach introduces the vibrational relaxation in terms of the vibrational autocorrelation function ϕ (11). Using stochastic theory the following expression may be derived (12):

$$\phi = \exp\left\{-\frac{|t|}{T_2} - \frac{\tau_c}{T_2}\left[\exp\left(-\frac{|t|}{\tau_c}\right)-1\right]\right\} \quad (1)$$

Two time constants, τ_c and T_2 are introduced in Eq. 1. The correlation time τ_c denotes the time scale of the dephasing mechanism. For $t \leq \tau_c$ the time dependence of ϕ is non-exponential with horizontal slope at $t=0$. For large t , Eq. 1 yields the desired exponential decay with dephasing time T_2 . Simple exponential dephasing considered previously (8) is contained in the present treatment for $\tau_c \rightarrow 0$. Experimental information on τ_c is highly desirable for the understanding of the dephasing mechanism. This can be achieved measuring the vibrational excitation by coherent Raman scattering of delayed probing pulses.

We have carried out numerical calculations of the molecular excitation by stimulated Raman scattering and of the coherent Raman probe scattering using the more general description of vibrational dynamics connected with Eq. 1. Our results are briefly summarized as follows: (i) Keeping the spectroscopic linewidth $\delta\nu$ constant (FWHM of the Fourier transform of Eq. 1) we note only little effect of τ_c on the stimulated amplification of the Stokes pulse of the pumping process. (ii) The time evolution of the vibrational excitation and of the coherent probe scattering signal, however, are notably effected by τ_c . (iii) For experimental investigations special conditions appear to be advantageous excitation by stimulated Raman scattering with small amplification factor $G \approx 2$ and distinct frequency shift of the stimulated excitation process $\Delta\nu = \nu_L - \nu_S - \nu_O \approx 3 \delta\nu$.

We have devised a double-channel picosecond system for the direct measurement of τ_c , measuring the coherent probe scat-

tering signal $S^{\text{coh}}(t_D)$ of the vibrational transition and the instrumental response curve $R(t_D)$ under identical geometrical conditions. With this system we have investigated several CH_2 - and CH_3 -stretching modes in the neat liquid at room temperature (10). Data on the symmetric ν_1 -mode at 2987 cm^{-1} of CH_2BrCl are presented in Fig. 3. A small amplification of the incident Stokes pump pulse by a factor of $G = 1.6 \pm .4$ has been adjusted for the excitation process. The normalized probe scattering signal, $N^{\text{coh}}(t_D)$, is plotted versus delay time t_D , which represents the ratio of the coherent probe scattering signal $S^{\text{coh}}(t_D)$ to the reference signal $R(t_D)$ measured at the same delay setting. Values of $N^{\text{coh}} \neq 1$ reflect the delayed response of the vibrational transition via time constants τ_c and T_2 .

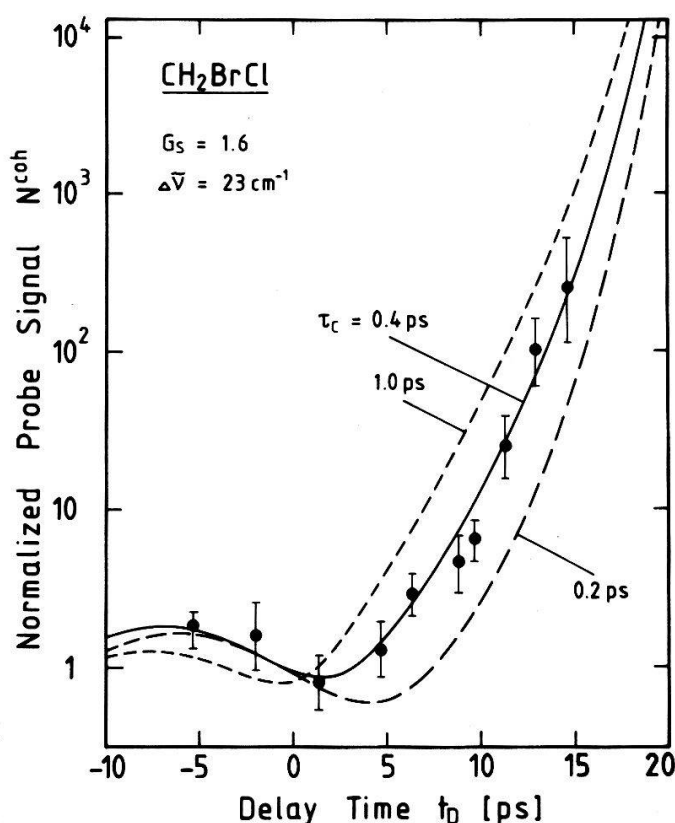


Figure 3. Normalized probe signal $N^{\text{coh}}(t_D)$ versus delay time t_D for the ν_1 - CH_2 -mode of neat CH_2BrCl ; experimental points; theoretical curves

The solid curve in Fig. 3 has been calculated for $\tau_c = 0.4$ ps and $T_2 = 1.5$ ps. The latter value is consistent with the observed asymptotic time dependence of the scattering signal $S^{\text{coh}}(t_D)$. The good agreement with the experimental points should be noted. The results for τ_c and T_2 are in excellent accordance with data on the spontaneous Raman linewidth. For comparison, two broken lines are also shown in the Fig. which are calculated for constant $\delta\nu$ and values of $\tau_c = 0.2$ ps and 1.0 ps, respectively; these curves notably deviate from the experimental points. The data of Fig. 3 present clear evidence for a finite time scale, $\tau_c > 0$, of the dephasing interaction.

Similar data were obtained for the ν_1 -stretching modes of CH_3I and CH_3CN yielding values of $\tau_c = 0.5$ and 0.7 ps, respectively. The time constants in the subpicosecond range indicate that the relaxation mechanism occurs close to the limit of homogeneous broadening. Our results represent the first time domain observation of non-exponential vibrational relaxation. Assuming dephasing via the repulsive part of the intermolecular potential to be predominant, the constant τ_c represents the time scale of translational motion; i.e. the elastic collision time. Simple models of the liquid state suggest this time to be 10^{-12} to 10^{-13} s in satisfactory agreement with our experimental data.

In conclusion we point out that we have investigated the population decay of the ν_1 -modes of CH_2 -halides. Comparison of the measured lifetimes with theoretical estimates gives evidence for rapid V-V transfer. Using overtone absorption we show that higher excited vibrational levels can be directly populated for the study of population decay and energy transfer.

We have also observed the time constant τ_c of vibrational relaxation in liquids. Our time domain observations are consistent with spectroscopic data (13) and demonstrate that the dephasing interaction proceeds on the subpicosecond time scale.

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