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Direct Measurement of the Vibrational Lifetimes of Molecules in Liquids

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A normal molecular vibration is strongly excited by a picosecond light pulse. The rise and decay of the excess population of the first excited vibrational state (electronic ground state) is observed with a delayed probe pulse. These measurements give, for the first time, values of the lifetimes of molecular vibrations in liquids.

During the past decades an extensive literature has been accumulated on the normal vibrational modes of molecules.[1,2] In liquids, the Raman and infrared frequency spectra, the degree of polarization, the intensity ratios, and—to a lesser degree—the linewidths have been studied for numerous polyatomic molecules. There is one material parameter which has received little attention: the lifetimes of molecular vibrations in liquids, τ'. In fact, there exists no experimental technique which allows the determination of the lifetime of a well-defined vibrational mode in liquids.[3] In the past, very rough estimates were made from measurements of the ultrasonic dispersion and absorption.[4] More recently, fluorescence measurements were reported involving electronic vibrational states of dissolved highly complex dye molecules.[5] Previous work, including theoretical considerations, suggested that the values for the lifetimes should be between 10^{-10} and 10^{-12} sec.

In this Letter we wish to present measurements of the vibrational lifetimes τ' in liquids. Intense molecular vibrations are excited by a powerful short pump pulse via stimulated Raman scattering. An increase in the population of the excited vibrational state is produced which gives rise to enhanced incoherent anti-Stokes Raman scattering of a second short light pulse (of different frequency). Varying the delay time between pump pulse and probe pulse, the rise and decay of the excess density of excited molecules is observed. The decay of the scattering signal is a direct measure of τ'.

We believe that our investigations represent the first measurements of the vibrational lifetimes of simple normal modes of polyatomic molecules in liquids.

We have made a detailed study of the development of the molecular excitation by transient stimulated Raman scattering. Our starting differential equations for the Stokes light field E_S, the amplitude Q of the vibrational field, and the population probability n of the molecular excitation have been discussed in the literature[6,7]:

$$\frac{\partial E_S}{\partial z} \; \frac{1}{\upsilon_S}\frac{\partial E_S}{\partial t} = \frac{i\pi\omega_S{}^2 N}{c^2 k_S}\frac{\partial \alpha}{\partial Q} Q^* E_{L1}, \tag{1}$$

$$\frac{\partial Q}{\partial t} + \frac{Q}{2\tau} = \frac{i}{4m\omega_0}\frac{\partial \alpha}{\partial Q} E_{L1} E_S{}^*(1-2n), \tag{2}$$

$$\frac{\partial n}{\partial t} + \frac{n}{\tau'} = \frac{i}{8\hbar}\frac{\partial \alpha}{\partial Q}(E_{L1}E_S{}^*Q^* - E_{L1}{}^*E_S Q), \tag{3}$$

where E_{L1} is the pumping laser field, υ_S denotes the group velocity, k_S is the wave vector of the Stokes field with frequency ω_S; ω_0 and m are the frequency and the reduced mass of the specific vibration, respectively, N is the number of molecules per cubic centimeter, and $\partial\alpha/\partial Q$ represents the change of polarizability with vibrational amplitude. The time constants τ' and τ are of special interest here. It is readily seen from Eq. (3) that the value of τ' determines the lifetime of the molecular excitation (nN is the number of excited molecules per unit volume). Equation (2), on the other hand, shows that the dephasing time τ governs the decay of the coherent vibrational field Q. The time constants τ' and τ correspond to T_1 and T_2 in the Bloch equations, respectively.

The following points should be noted: (i) In deriving Eqs. (1) to (3) a two-level system is considered. Higher vibrational states ($v \geq 2$) can be neglected in our molecules on account of vibrational anharmonicities. (ii) The thermal equilibrium population is assumed to be negligible ($n_T \ll 1$), i.e., $\hbar\omega_0 \gg kT$. (iii) The approximations of small conversion efficiency of laser light to Stokes light (i.e., $E_{L1} = \text{const}$) and of small molecular excitation ($n \ll 1$) are made. It is easily seen from Eq. (2) that for $n \ll 1$ the second term on the right-hand side of the equation may be neglected, allowing the solution of Eqs. (1) and (2) independent of Eq. (3). It will be shown below that the assumptions (i) to (iii) hold well for our experimental situation. The solutions of

Eqs. (1) and (3) are obtained as follows: The Stokes field $E_S(t,z)$ and the vibrational field $Q(t,z)$ are evaluated numerically from Eqs. (1) and (2).[7] Then, the degree of molecular excitation $n(t,z)$ is calculated with the help of Eq. (3).

Experimentally, we observed the incoherent anti-Stokes Raman scattering of the probe pulse at 90° scattering angle. The delay time between pump and probe pulse is called t_D. The interaction of the excited molecules and the probing field E_{L2} yields the incoherent anti-Stokes Raman signal

$$S^{\mathrm{inc}}(t_D)=\frac{3\omega_{\mathrm{AS}}{}^3N^2A\Omega}{8\pi c^3\rho}\left(\frac{\partial\alpha}{\partial Q}\right)^2\int dz\,dt\,n(t,z)\times|E_{L2}(t-t_D,z)|^2, \qquad (4)$$

where ω_{AS} is the anti-Stokes frequency, ρ the density, A the beam cross section, and Ω the solid angle of acceptance. Equation (4) represents a convolution of the molecular excitation and the probing light pulse.

The scattering signal $S^{\mathrm{inc}}(t_D)$ corresponds to spontaneous anti-Stokes Raman scattering under nonequilibrium conditions. The population n of the excited vibrational state is above the thermal equilibrium value; n is determined by the external pumping process. The following numbers are typical for our investigations; they illustrate the molecular excitation achieved and the scattering signal $S_{\mathrm{max}}{}^{\mathrm{inc}}$ expected. For a single laser pulse of ~10 mJ energy and a Stokes conversion efficiency of several per cent,[8] we calculate a total number of excited molecules of approximately 5×10^{15}. The molecular excitation occurs in a small volume of $V\simeq10^{-3}$ cm^3 close to the exit window of the Raman sample (effective length $\Delta z\simeq4\times10^{-2}$ cm,[8] beam cross section $A\simeq3\times10^{-2}$ cm^2). For a number density of $N\simeq5\times10^{21}$ cm^{-3}, we obtain a maximum vibrational population of $n\simeq10^{-3}$ generated in the pumping process. This number should be compared with the thermal equilibrium population n_T. For example, for the CH vibrations at $\omega_0/2\pi c\simeq3000$ cm^{-1} in organic liquids, we calculate from the Bose factor $n_T=[\exp(\hbar\omega_0/kT)-1]^{-1}\simeq10^{-6}$. Note that n exceeds the equilibrium value n_T by 3 orders of magnitude. By using a probe pulse of ~0.5 mJ, the 5×10^{15} excited molecules give rise to a maximum signal of ~10^4 anti-Stokes photons, which are incoherently scattered into the solid angle $\Omega\simeq0.2$ sr. Scattering signals of this order of magnitude are readily detected with photomultipliers.

Our experimental system (Fig. 1) consists of a mode-locked Nd:glass laser, an optical shutter to cut a single picosecond pulse out of the pulse train, and an optical amplifier. A careful analysis of our pulses has been carried out and discussed in previous publications.[9,10] In short, we have single pulses with defined pulse duration and pulse shape, and without subpicosecond structure. The pulse ($B1$) enters the measuring cell and traverses the sample, generating intense molecular vibrations and Stokes-shifted light. The laser ($\omega_{L1}/2\pi c=9455$ cm^{-1}, corresponding to $\lambda\simeq1.06$ μm) and the Stokes light ($\omega_S=\omega_{L1}-\omega_0$, at $\lambda\simeq1.5$ μm, depending upon the sample) are measured by a fast photocell $P1$ and an infrared detector (Ge-Au) $P4$, respectively. They allow an estimate of the conversion efficiency, which was kept at a value of several percent to stay within the validity of our calculations. The potassium dihydrogen phosphate (KDP) crystal in the beam generates an additional light pulse at the second-harmonic frequency ($\omega_{L2}/2\pi c=18\,910$ cm^{-1}, corresponding to $\lambda\simeq0.53$ μm) which serves as a probe pulse with variable delay t_D. The optical delay between probe and pump pulse was carefully determined from the group velocities for the various optical components. The accuracy of the t_D scale is better than 5% while the absolute setting of $t_D=0$ is known to approximately 2 psec. The probe pulse interacts with the excited molecules in the Raman sample, and the inocherent anti-Stokes Raman signal is observed at 90° scattering angle with the help of efficient dielectric filters and the photomultiplier $P3$. Without external molecular excitation (pump beam blocked), the probe pulse

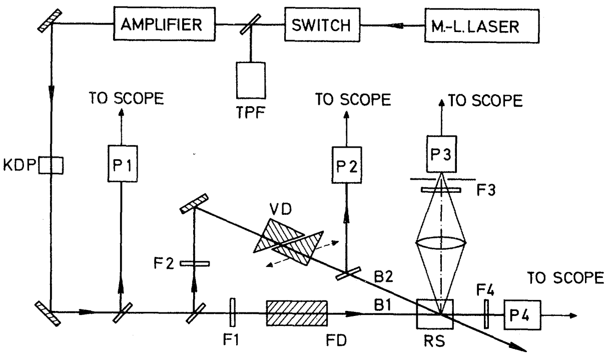

FIG. 1. Schematic of the experimental system. The pump beam $B1$ at $\lambda\simeq1.06$ μm and the probe beam $B2$ at $\lambda\simeq0.53$ μm interact in the Raman sample $\boldsymbol{RS}$. Glass rod for fixed optical delay, $\boldsymbol{FD}$; glass prisms for variable delay, VD; filter, F; photodetector, $\boldsymbol{P}$; two-photon–fluorescence system, $\boldsymbol{TPF}$.

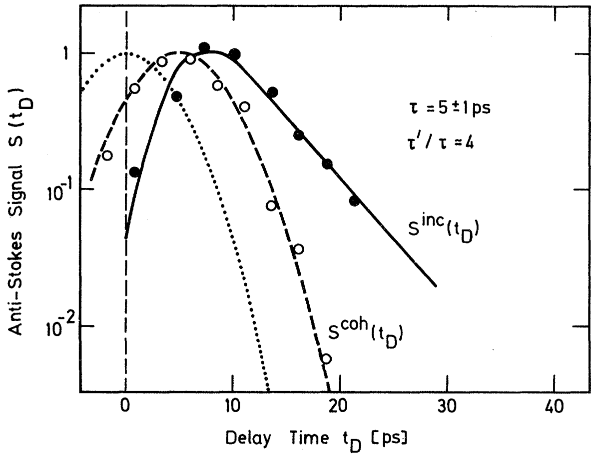

FIG. 2. Measured incoherent scattering signal $S^{\mathrm{inc}}(t_D)/S_{\max}^{\mathrm{inc}}$ (closed circles) and coherent scattering $S^{\mathrm{coh}}(t_D)/S_{\max}^{\mathrm{coh}}$ (open circles) versus delay time t_D between pump pulse and probe pulse for 1, 1, 1-trichlorethane. The solid and the dashed curves are calculated. The dotted line indicates the pump pulse.

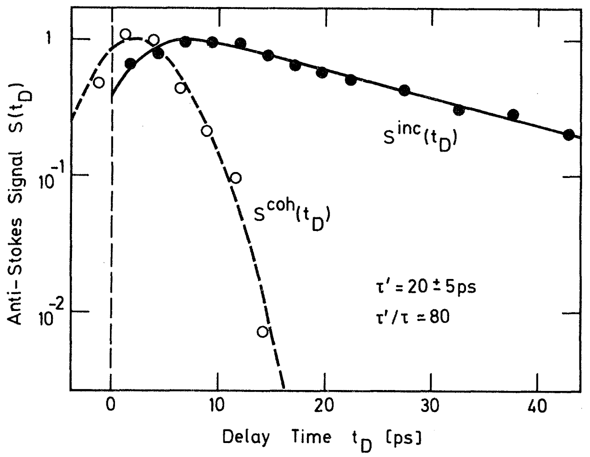

FIG. 3. Measured incoherent scattering $S^{\mathrm{inc}}(t_D)/S_{\max}^{\mathrm{inc}}$ (closed circles) and coherent scattering $S^{\mathrm{coh}}(t_D)/S_{\max}^{\mathrm{coh}}$ (open circles) versus delay time t_D for ethyl alcohol. The solid and dashed curves are calculated (see text).

showed no anti-Stokes scattering signal. Spontaneous anti-Stokes Raman scattering was below the limit of detectibility on account of the small thermal equilibrium population of the vibrational state.

We have investigated the totally symmetric CH_3 valence-bond vibration at $\omega_0/2\pi c = 2939$ cm^{-1} in 1, 1, 1-trichloroethane and the CH_3 vibration at $\omega_0/2\pi c = 2928$ cm^{-1} in ethyl alcohol at 300°K. Figures 2 and 3 present our experimental results. The anti-Stokes signal $S^{\mathrm{inc}}(t_D)$ of the probe beam is plotted versus delay time t_D. The experimental points (closed circles) are average values obtained from approximately ten different measurements. The signal-to-background ratios were 20 and 5 for CH_3-CCl_3 (Fig. 2) and C_2H_5OH (Fig. 3), respectively. The scattering signal rises to a maximum which is well shifted with respect to the pump pulse (dotted line in Fig. 2). The maximum vibrational population is reached shortly after the peak of the pump pulse, since time is required for the pumping process to accumulate the molecular excitation. For longer delay times the signal decreases according to the vibrational lifetime τ'. The signal decay is well accounted for by an exponential slope (note the logarithmic scale at the ordinate) which allows the direct determination of τ'. From Fig. 2 we find $\tau' = (5 \pm 1)\times 10^{-12}$ sec for CH_3CCl_3. In the case of C_2H_5OH (Fig. 3) a vibrational lifetime $\tau' = (20 \pm 5)\times 10^{-12}$ sec is measured.

From infrared absorption data[11] the difference between the $v = 0 \rightarrow v = 1$ and the $v = 1 \rightarrow v = 2$ transitions is ~150 cm^{-1}. Since the frequency width of the pump pulse is 3 cm^{-1} and the Raman linewidths are 5 and 17.4 cm^{-1} for CH_3CCl_3 and C_2H_5OH,[12] respectively, the approximation of a two-level system is well justified. The solid curves in Figs. 2 and 3 are calculated as outlined above, using the measured values of τ' and the dephasing time τ discussed below. The theoretical curves fit our experimental data quite well at $t_D = 0$, at the position of the maximum, and for larger values of t_D. The comparison with theory confirms our values of the vibrational lifetimes of 5 and 20 psec for CH_3CCl_3 and C_2H_5OH, respectively.

We now turn to the discussion of the dephasing time τ of the two molecular vibrations investigated here. Figures 2 and 3 present our experimental data on τ. The experimental system for measuring this time constant has been described previously.[10] In these measurements a short light pulse probes the coherently excited vibrational field Q. The observed anti-Stokes Raman signal $S^{\mathrm{coh}}(t_D)$ is scattered under phase-matching conditions close to the forward direction. In Figs. 2 and 3 we plot the coherent scattering signal $S^{\mathrm{coh}}(t_D)$. For CH_3CCl_3, the $S^{\mathrm{coh}}(t_D)$ curve rises to a maximum at $t_D \simeq 5$ psec and decreases rapidly for larger values of t_D (see Fig. 2). In the case of C_2H_5OH (Fig. 3), the coherent signal $S^{\mathrm{coh}}(t_D)$ behaves similarly, with the maximum situated at $t_D \simeq 2$ psec. The rapid decay of the signal indicates the dephasing time τ to be smaller than 2 psec for both liquids.

The dashed lines in Figs. 2 and 3 are calculated curves, which account well for our experimental points. For CH_3CCl_3 the best fit by the theoretical curve is obtained for $\tau \simeq 1.3$ psec. Because of our comparatively long laser pulses ($t_p \simeq 8$ psec), we estimate our value of τ to be accurate to ± 50%. This value of $\tau \simeq 1.3$ psec compares satisfactorily with our measurements of the spontaneous Raman linewidth of $\Delta\omega/2\pi c \simeq 4.9$ cm^{-1}, which suggest $\tau \simeq 1.1$ psec. The dephasing time of ethyl alcohol is too short to be deduced from Fig. 3.[10] A value of $\tau \simeq 0.26$ psec is estimated from spontaneous Raman data. The dashed curve in Fig. 3 has been calculated using this value.

We are now in a position to compare our data on τ' and τ. It is most interesting to see that the measured data of $S^{\mathrm{inc}}(t_D)$ and $S^{\mathrm{coh}}(t_D)$ in Figs. 2 and 3 differ significantly.[13] The incoherent scattering is shifted to larger values of t_D and decays more slowly than the coherent signal curve, indicating different values of the time constants τ' and τ of the individual vibrational transition. For CH_3CCl_3 we find $\tau'/\tau \simeq 4$, whereas a value of $\tau'/\tau \simeq 80$ is estimated for C_2H_5OH. Our values of τ'/τ show clearly that phase relations between excited molecules relax more rapidly than does the vibrational energy. This result has been expected on account of the different physical mechanisms of the two relaxation processes. The transfer of vibrational quanta $\hbar\omega_0$ to neighboring molecules is a major factor for the value of τ, while the anharmonic terms of the molecular potential strongly effect τ'.

In conclusion we wish to say that our investigations open a new field for the study of molecular relaxations in liquids. Our method is readily extended to other substances, and with more refined techniques it can be applied to different vibrations of the same molecule. Measurements in pure and mixed liquids should give information on effects of molecular enviroment. We feel that the data on vibrational lifetimes will promote the understanding of molecular interactions in liquids.

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