

PICOSECOND TIME-RESOLVED MEASUREMENTS OF VIBRATIONAL ENERGY
TRANSFER AND RELAXATION PHENOMENA IN LARGE POLYATOMIC MOLECULES

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Abstract - Vibrational modes in the electronic ground state are investigated by recently developed ultrashort measuring techniques. Using tunable infrared pulses well defined vibrational states are first excited far above the thermal equilibrium value, and with delayed probe pulses the instantaneous population of various vibrational states is monitored. Rapid redistribution (1×10^{-12} sec) between neighboring energy states is seen in various molecules while the decay to lower vibrational levels is found to depend very strongly on the mode structure of the individual molecule. Population lifetimes of 1 psec and 40 psec are measured for CH_3 modes in CH_3I and ethanol, respectively.

In this short review, experimental studies are described which allow quite directly the investigation of a series of very rapid vibrational processes. Here we restrict ourselves to vibrational modes in the electronic ground state.

Fig. 1 gives somewhat schematically an outline of several experimental techniques which had to be developed in order to measure various new molecular parameters. Well-defined vibrational modes are excited by a first intense ultrashort laser pulse via stimulated Raman scattering or via direct resonance infrared absorption (left column of Fig. 1). A second interrogating pulse which is properly delayed with respect to the first exciting pulse monitors the instantaneous state of the excited vibrational system. Three different ways of probing (center of Fig. 1) give a variety of information (right column of Fig. 1).

(i) With coherent probing we measure the state of phase correlation within the excited volume. Time does not allow to discuss this topic here since it is not the main subject of the present talk. We briefly note that an important molecular parameter, the dephasing time of a specific vibrational mode, can be directly obtained by a coherent probing experiment.

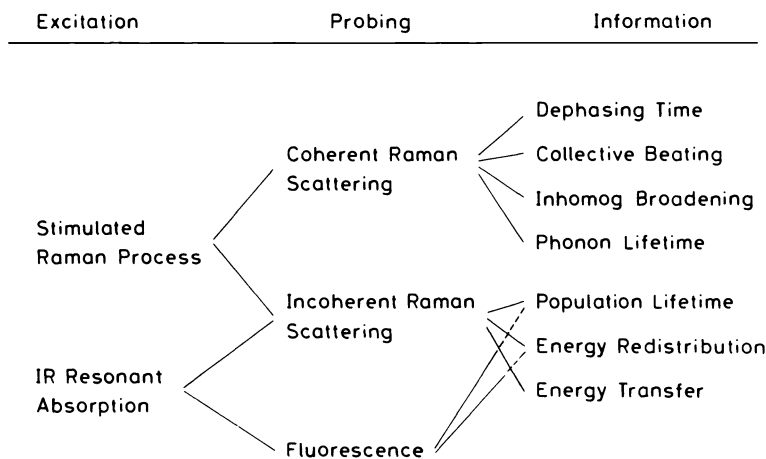


Fig. 1 Short outline of the paper. Two excitation processes allow to excite a specific vibrational mode. Three different probing techniques provide time resolved data on a variety of subjects listed on the right.

(ii) Of special interest for the present topic is the observation of the (spontaneous) anti-Stokes Raman signal of the interrogating probe pulse. This signal is a direct measure of the momentary degree of population of a specific vibrational state. With this technique it was possible for the first time to observe population lifetimes, energy transfer and vibrational redistribution of polyatomic molecules in the liquid state. We note that such data are - in most cases - not available from other experimental methods.

(iii) In highly diluted systems, it is possible to investigate the momentary occupation of a vibrational state by a recently developed fluorescence technique. The time delayed probe pulse promotes the excited molecules close to the bottom of the first excited singlet state. The degree of fluorescence from this latter state is directly proportional to the momentary occupation of the excited vibrational state in S_0 .

Before we present various experimental results, several short remarks should be made concerning the experimental system. We work with a Nd-glass laser system consisting of an oscillator and an amplifier. We know from various investigations that we have single pulses of 6 psec duration and a frequency bandwidth of 3 cm^{-1} , i.e., our pulses are very nearly bandwidth limited. Starting with these pulses we prepare new frequencies by second harmonic generation or - more interesting - by the three-photon parametric process. The latter technique allows to generate ultrashort infrared pulses over a substantial frequency range. With LiNbO_3 crystals and a pumping frequency of 9455 cm^{-1} a tuning range up to 2500 cm^{-1} is possible (LiNbO_3 absorbs at longer wavelengths).

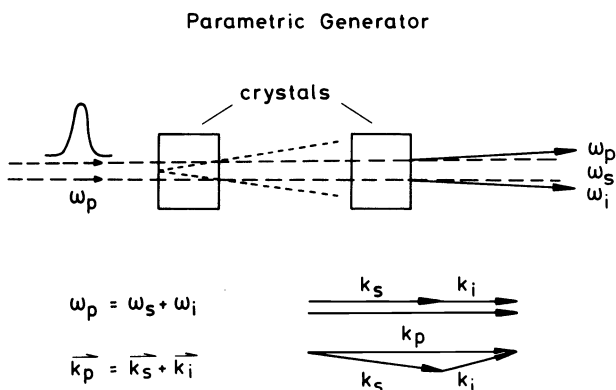


Fig. 2 Schematic diagram of parametric generator set-up. The incident pump pulse generates a parametric emission in the first crystal which is used as an input signal for the amplification process in the second specimen.

Picosecond Pulses in the Infrared

Tunability	2500 to 7000 cm^{-1}
Frequency Width	8 cm^{-1}
Pulse Duration	3 psec
$t_p \times \Delta \nu =$	0.7
Divergence	3×10^{-3} rad
Intensity	$\sim 10^9 \text{ W/cm}^2$
Energy Conversion	$\sim 5\%$

Fig. 3 Table of pulse properties generated by the parametric generator scheme.

We have spent considerable effort to obtain a small bandwidth of the infrared pulses in the parametric process. The two-crystal technique depicted in Fig. 2 produces infrared pulses which come close to the Fourier transform limit. As indicated in Fig. 2, the first crystal acts as a frequency generator of large divergence and correspondingly large bandwidth while the second crystal, placed at a distance of approximately 40 cm from the first crystal, amplifies only the small frequency band in the center of the pump beam. The experimental data of our IR-pulses are summarized in Fig. 3. The parametric process shortens somewhat the pulse duration and, more important, steepens the wings of the pulse on account of the nonlinear parametric generation process. In Fig. 4, our experimental system is depicted schematically. The powerful laser pulse

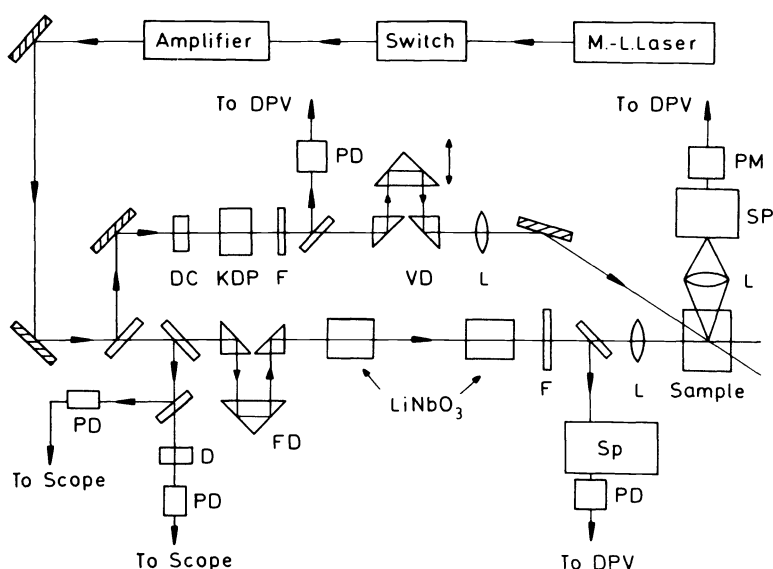


Fig. 4 Experimental system used to measure energy relaxation times. A single picosecond laser pulse generates either stimulated Raman scattering in the sample or produces ultrashort infrared pulses when the two nonlinear crystals (broken line) are inserted. The infrared frequency is tuned by crystal rotation. The probe pulse travels through the upper delay system and interrogates the excited volume. With spectrometer (SP) and photomultiplier (PM) a spontaneous anti-Stokes signal or a fluorescence signal can be measured. The input intensity is determined by two fast photodiodes (PD) in conjunction with a nonlinear absorber (D).

enters the two parametric crystals from the left and the generated infrared light excites the sample located at the lower right of the Figure. A beam splitter in the input beam produces the second interrogating pulse which is transformed to the second harmonic frequency in a KDP crystal. After a proper delay, both pulses meet in the same volume of the specimen. The anti-Stokes Raman signal or the generated fluorescence is monitored by a spectrometer in conjunction with a photomultiplier. We have studied a variety of molecules and vibrational modes and found a wide range of population lifetimes. Two examples should be discussed here.

First we present experimental data on ethanol. A CH-stretching mode of the molecule was excited by an infrared pulse of $\nu = 2930 \text{ cm}^{-1}$ and the anti-Stokes Raman signal with the same frequency shift was measured. The experimental curve of Fig. 5 suggests two time constants. The first rapid decay of the primary scattered signal is interpreted as being due to a redistribution of vibrational energy between neighboring energy states, while the following slow decay corresponds to the decay to lower energy states. In fact, the subsequent occupation of the bending modes at $\sim 1500 \text{ cm}^{-1}$ has been observed in an earlier experiment. Fig. 6 shows the energy levels of ethanol and the energy states which are involved in the excitation and decay processes of our experiment. Note the numerous energy states around 3000 cm^{-1} which have smaller effective

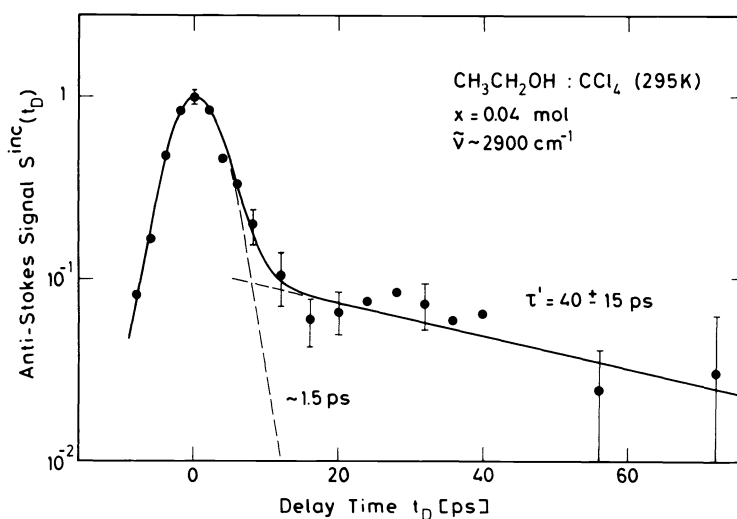


Fig. 5 Incoherent anti-Stokes probe signals with frequency shift of ~ 2900 cm⁻¹ versus delay time. Sample: 4 mol per cent CH₃CH₂OH in CCl₄. The CH₃-stretching mode was excited by an infrared pulse. The first fast signal decay is related to rapid energy redistribution between neighboring energy states. The slower decay corresponds to energy relaxation to lower bending modes.

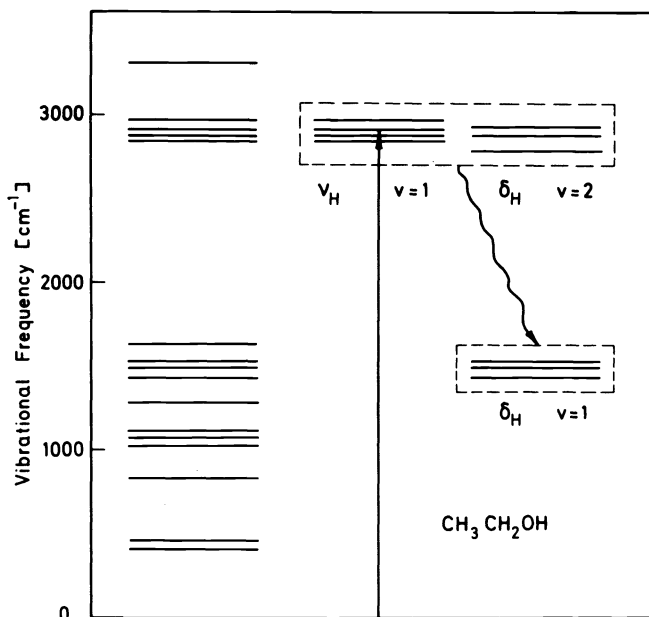


Fig. 6 Schematic diagram of vibrational states of ethanol. A CH stretching mode is excited by the infrared pump pulse after energy redistribution among the neighboring overtones of the CH bending modes (time constant 1.5 psec). A much slower decay was observed to the bending modes around 1400cm⁻¹.

Raman cross sections than the primary excited mode. The subsequent decay to the lower bending modes is indicated. Quite different from the preceding case is the vibrational energy decay in a relatively small molecule CH₃I. Two experiments were performed (see Fig. 7). First, the symmetric CH₃ stretching mode (ν_1) was measured; then the asymmetric CH₃ stretching mode (ν_4) was ex-

cited at 3050 cm^{-1} and the instantaneous occupation of the lower ν_1 level was measured as a function of time. In both cases we find an energy decay of approximately 1 psec indicating rapid depopulation of the excited vibrational states. We emphasize that in the second experiment the position of the excitation maximum is only slightly shifted by approximately 1 psec indicating very rapid energy exchange between the ν_1 and ν_4 levels. Recent calculations by

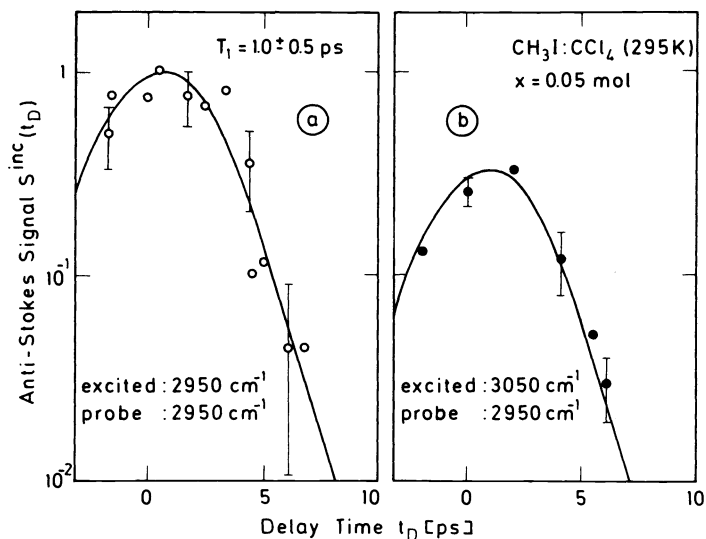


Fig. 7 Incoherent anti-Stokes signals of CH_3I measured at a frequency shift of 2950 cm^{-1} . (a) The molecule is excited by an infrared pulse of $\nu = 2950\text{ cm}^{-1}$ (open circles). (b) The infrared pumping pulse has a frequency of $\nu = 3050\text{ cm}^{-1}$ exciting the highest vibrational mode of CH_3I . Note the small time delay necessary for energy exchange.

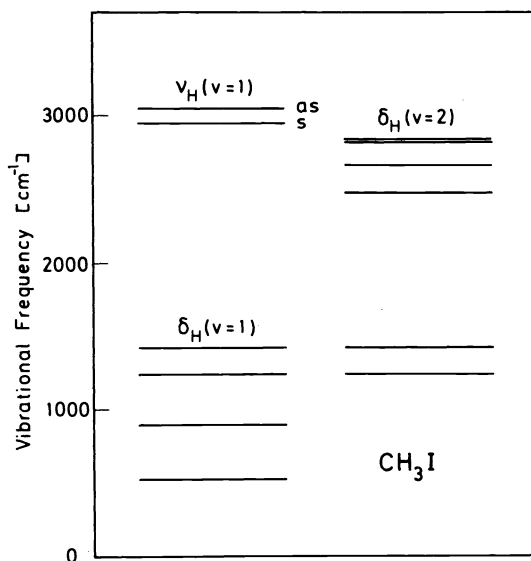


Fig. 8 Vibrational energy states of CH_3I . In our investigations (see Fig. 7), the symmetric or asymmetric CH_3 stretching mode was excited by the infrared pump pulse and the excess population of the symmetric mode was monitored as a function of time. We observe energy redistribution between the two levels with a time constant of 1.5 psec.

S. Fischer et al. of our Department suggest strong coupling between the ν_1 and ν_4 levels and strong mixing between the two CH_3 levels and the $2\nu_5$ state. The theoretical results are in good agreement with the short time constants reported here. Fig. 8 shows the energy states of CH_3I related to our investigation. The most important levels, the two CH_3 modes and the overtone of the bending mode ν_5 , are indicated.

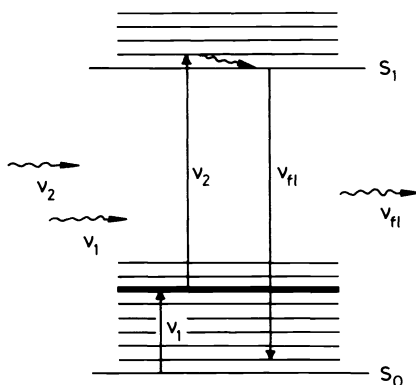


Fig. 9 Double-resonance fluorescence probing technique. Schematic diagram of the relevant molecular energy states. Vibrational level (2) is excited by an infrared pulse of frequency ν_1 . The time dependence of the population of level (2) is monitored with a second delayed pulse of frequency ν_2 . The (integrated) fluorescence at ν_{fl} is a measure of the population lifetime T_1 of level (2).

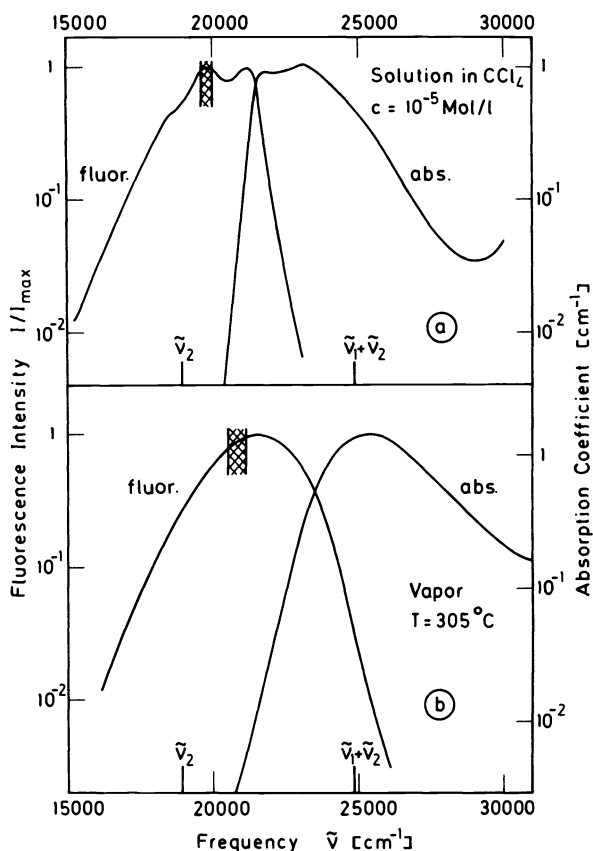


Fig. 10 Absorption and fluorescence of coumarin 6 molecules: (a) Liquid solution of 10^{-5} mol/liter in CCl_4 and (b) vapor phase at 305°C (1 torr). The frequency $\nu_1 + \nu_2$ (infrared pulse + green pulse) is indicated at the abscissa.

Now we turn to the two-step frequency excitation with observation of the generated fluorescence. Fig. 9 shows very schematically the energy levels involved in this technique. The infrared pulse of frequency ν_1 excites a vibrational level in the S_0 state above its thermal equilibrium value. A second pulse at a (visible) frequency ν_2 pumps the excited molecules to the fluorescent S_1 state. The fluorescence is observed as a function of delay time between the two pulses. In Fig. 10 we show the absorption and fluorescence spectra of coumarin 6, a relatively large molecule consisting of 42 atoms (see top of Fig. 11). In the upper part of Fig. 10 we see results of a 10^{-5} molar solution of coumarin 6 in CCl_4 . The broad bands are typical for dye molecules of the size investigated here. In the lower part of Fig. 10, the spectra of coumarin 6 vapor at 300°C are depicted. The corresponding vapor pressure was measured to be one torr. A similar shift of absorption at higher temperature has been reported for similar molecules. In a first experiment, we measured the relaxation time of coumarin 6 in CCl_4 solutions after excitation of vibrational states at 2970 cm^{-1} . We found a very short time constant of close to 1 psec. Subsequently, we excited a vibrational overtone at 6000 cm^{-1} in a coumarin vapor at 305°C and observed a time constant of 4 psec only (see Fig. 11). There are two

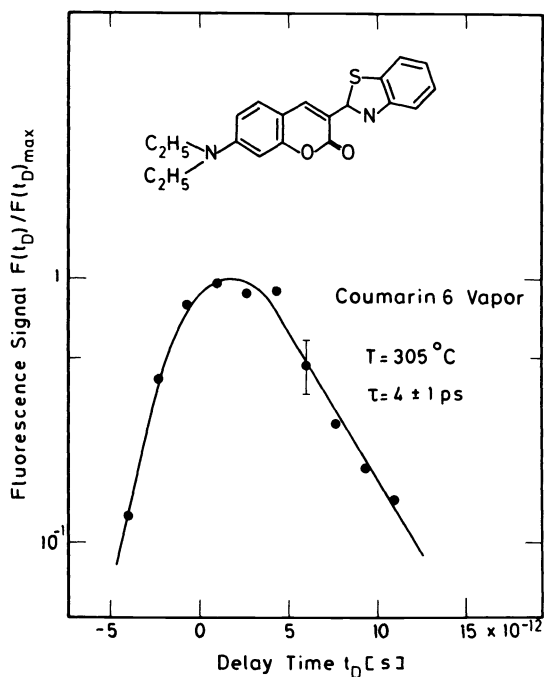


Fig. 11 Vibrational relaxation time of coumarin 6 in the vapor at 305°C . An overtone at 5950 cm^{-1} is primarily excited by an infrared pulse. The fluorescence, produced by the probe pulse, is plotted versus delay time between the excited infrared and probing green pulse. The exponential decay of the signal gives a population lifetime of 4 ± 1 psec. Top: The coumarin 6 molecule.

possibilities for the rapid decay of our signal: Fast redistribution between neighboring energy states with smaller effective Franck-Condon factors and quick vibrational energy decay to lower vibrational states. In any case, the fast time constant in a collision-free gas system is an interesting observation which has not been reported previously.

In summary, we wish to say that we are very much at the beginning. Nevertheless, our measurements indicate quite clearly the potential of determining ultrafast vibrational processes with picosecond infrared light pulses.

For details the reader is referred to the following papers:

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