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Picosecond Lifetimes and Efficient Decay Channels of Vibrational Models of Polyatomic Molecules in Liquids

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Convincing evidence is presented that anharmonic coupling between fundamental vibrational modes and overtones or combination modes is of major importance for the lifetime of vibrational states. The selection rules known to hold for Fermi resonance determine the decay channels. In a number of examples the decay pathways of vibrational energy were observed experimentally by measuring the population and depopulation of subsequent vibrations. Drastic variations of vibrational lifetimes were found for different vibrations of the same molecule.

Molecules are first excited by an ultrashort resonant infrared pulse and the instantaneous degree of excitation is monitored by observing the anti-Stokes Raman signal of a delayed probe pulse. Different vibrational modes are distinguished by their characteristic anti-Stokes frequency.

We have investigated numerous molecules and found widely varying values of the population life-times between 1 ps and 240 ps in polyatomic molecules at room temperature /1,2/. Special attention was paid to the CH-stretching modes in the frequency range of 3000±100 cm^{-1}.

Vibrational energy is transferred from the CH-stretching modes ($\sim$3000 cm^{-1}) via overtones and combination modes to lower energy states. Intramolecular anharmonic coupling, the Fermi resonance, manifests itself in the infrared and Raman spectra. Overtones and higher order combination modes borrow intensity from CH-stretching modes. We define as a measure of Fermi-resonance mixing the intensity ratio, R, between the final and initial state taken from the infrared or Raman spectrum. In a recent publication a formula was derived which allows to estimate the life time T_1 of vibrational states:

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

N corresponds to the number of states initially excited, R is a measure of the Fermi resonance, and $T_2(f)$ stands for the dephasing time of the final state. $T_2(f)$ may be estimated from the Raman line-width $\Delta\tilde{\nu}$ as $T_2(f) = (2\pi c \Delta\tilde{\nu})^{-1}$ ($T_2(f)$ is equal to $T_2/2$ measured in coherent Raman experiments) . The frequency ω represents the energy difference between the initial and final state. Ω has a value close to 100 cm^{-1}.

As an example for the importance of Fermi resonance we present data of the two molecules 1,1-dichloroethene and trans 1,2-

dichloroethene which are made up of the same atoms; only two atoms have exchanged their positions. The infrared and Raman spectra between 2950 cm^{-1} and 3250 cm^{-1} of both molecules are depicted in Fig.1. There are drastic differences in the anharmonic coupling of the CH-stretching modes. In Fig.1a we see strong Fermi resonance of $CH_2=CCl_2$ between the fundamental ν_1 and $\nu_2+\nu_3$, both of A_1 symmetry and between the fundamental ν_7 and $\nu_2+\nu_6+\nu_{11}$, both of B_1 symmetry /3/. This observation suggests that we have to consider at least two decay channels for the CH_2-stretching modes. For the decay $\nu_1 \rightarrow \nu_2+\nu_3$ we estimate the intensity ratio $R = 0.2\pm0.05$ and calculate $T_2(f) = 0.3$ ps from the Raman linewidth of $\Delta\tilde{\nu} = 17$ cm^{-1}. With $\tilde{N}=1$ and $\omega = 45$ cm^{-1} we calculate from (1) a value of $T_1 = 4\pm2$ ps. For the second decay channel $\nu_7 \rightarrow \nu_2+\nu_6+\nu_{11}$ we have to take a short dephasing time $T_2(f)$ of the combination mode. We estimate $T_2(\nu_2+\nu_6+\nu_{11}) \approx 0.2$ ps from the observed line width. With $R = 0.6\pm0.1$, $\tilde{N}=1$ and $\omega = 45$ cm^{-1} we calculate $T_1 = 1.5$ ps.

According to Figs.1a and 1b the symmetric (ν_1) and asymmetric (ν_7) CH_2-stretching vibrations are separated by 100 cm^{-1}. We estimate an energy-transfer time between the CH_2-stretching modes of $T_1(\nu_1 \rightarrow \nu_7) \approx 3.3$ ps using the formula $T_1(\omega_1 \rightarrow \omega_7) = T_2(\omega_1)\exp(\omega/\Omega)^{2/3}$, where $T_2(\omega_1)$ was taken from the Raman spectrum.

The estimates given here indicate that vibrational energy flows faster out of the ν_7 mode than it is supplied by the transfer $\nu_1 \rightarrow \nu_7$. For the excited and interrogated mode ν_1 we simply add the two decay rates for the two decay channels $\nu_1 \rightarrow \nu_7$ and $\nu_1 \rightarrow \nu_2+\nu_3$ and arrive at a lifetime $T_1(\nu_1) \approx 2$ ps.

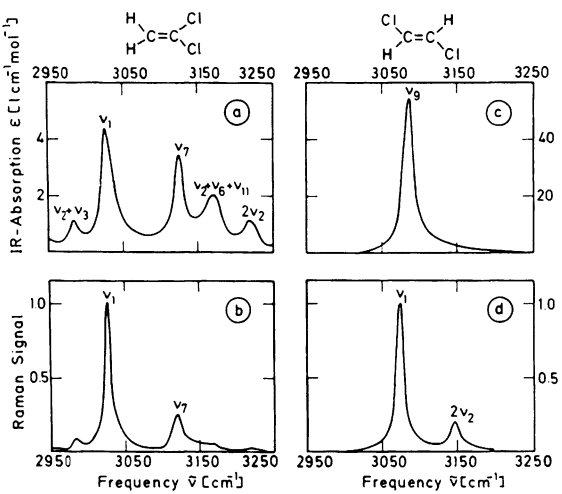

Fig.1 Infrared absorption (a) and Raman (b) spectra of CH_2CCl_2 between 2950 and 3250 cm^{-1}. Two combination tones are in strong Fermi resonance with the two CH-stretching modes ν_1 and ν_7. Infrared absorption (c) and Raman (d) spectra of trans CHClCHCl. There is less Fermi-resonance mixing than in CH_2CCl_2.

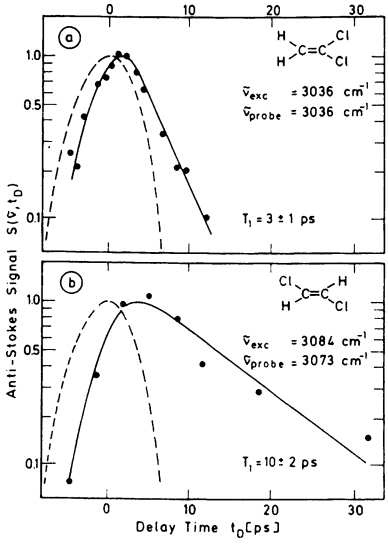

Fig.2 Anti-Stokes scattering signal versus delay time of the probing pulse. (a) CH_2CCl_2 in CCl_4 (c = 0.35 m.f.). The decay of the CH_2-stretching mode at 3036 cm^{-1} is shown. (b) trans CHClCHCl in CCl_4 (c = 0.35 m.f.). The CH-stretching mode at 3084 cm^{-1} is excited and the mode at 3073 cm^{-1} is monitored. The broken curves are the cross-correlation functions of the IR exciting and green probing pulses.

In Fig.2a we present experimental data of the direct determination of the T_1 value. The scattered Raman signal of the ν_1 mode rises to a slightly delayed maximum during the excitation process and decays with a relaxation time of T_1 discussed in the preceding paragraph. The broken curves in Fig.2 are cross-correlation curves of the excitation and probing pulse; they determine the zero point on the time axis and give a good indication of the time resolution of the experiment.

In Fig.1c we see the infrared active CH-stretching mode ν_9 and in Fig.1d the Raman active symmetric ν_1 mode of trans CHClCHCl Here we find a considerably smaller Fermi resonance. The Raman spectrum of Fig.1d suggests some anharmonic coupling between ν_1 and $2\nu_2$, both of A_g symmetry /3/. With the values R = 0.15±0.02, T_2 = 0.3 ps, N=2 and ω = 80 cm^{-1} we calculate T_1 = 13 ps. It should be noted that there might be additional weak Fermi resonance between the ν_9 mode and higher combination modes (e.g. $\nu_2+\nu_5+\nu_{10}$) burried under the high frequency tail of the ν_9 fundamental. These additional decay channels may reduce somewhat the estimated T_1 value.

The time dependence of the CH-stretching modes of trans CHClCHC is depicted in Fig.2b. The 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 population of the ν_1 mode, gives

clear evidence of the quick energy exchange between the two CH fundamentals ν_1 and ν_9. The decay of the signal curve suggests a long lifetime of the two CH-stretching modes of T_1 = 10±2 ps. This number is in good agreement with the value estimated above. The small intramolecular coupling gives rise to the longer vibrational life time.

The vibrational states of acetylene are well documented in the literature /4/. Inspection of the energy-level system (see Fig.3) suggests the following interesting situations: (i) Energy in the high lying CH-stretching modes around 3200 cm^{-1} readily flows into several combination modes, all of which comprise the symmetric C≡C-stretching mode at ν_2 = 1968 cm^{-1}. (ii) The energy transfer from the ν_2 mode to neighboring combination modes is forbidden by symmetry selection rules. Thus we expect a long population life-time of the ν_2 mode.

Experimentally we investigated a solution of C_2H_2 in CCl_4. Acetylene molecules first are vibrationally excited via the infrared active CH-stretching mode ν_3 = 3287 cm^{-1} and the population and depopulation of the ν_2 mode at 1968 cm^{-1} is monitored. In Fig.4 we indeed see a rapid population of the ν_2 mode within ≤ 3 ps and a very slow depopulation with a time constant of 240 ps. The ν_2 mode in acetylene represents a bottle-neck state. It exhibits the longest relaxation time observed so far in a polyatomic molecule in the liquid state at room temperature.

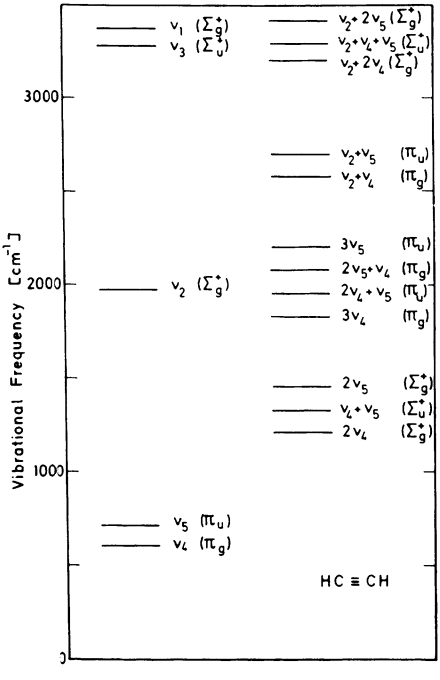

Fig.3 Energy-level diagram of Acetylene

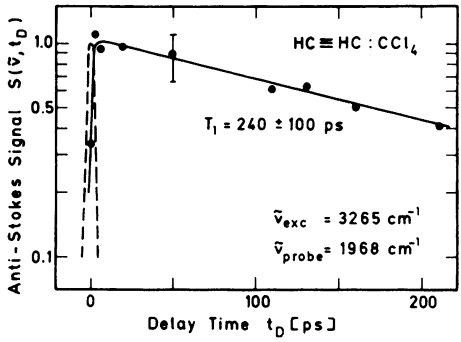

Fig. 4 Anti-Stokes scattering signal of C_2H_2 in CCl_4 versus delay time. Excitation frequency is 3265 cm^{-1}. The decay of the C≡C mode at 1968 cm^{-1} is monitored.

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