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CHANGES OF VIBRATIONAL LIFETIMES WITH MINOR STRUCTURAL MODIFICATION OF SMALL POLYATOMIC MOLECULES

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Substantial changes of population lifetimes of CH-stretching modes are observed when two atoms are exchanged in $CH_2{=}CCl_2$ to form trans CHCl=CHCl and when three deuterons are substituted in C_6H_6 to form 1,3,5-$C_6H_3D_3$. The measured lifetimes are in good agreement with estimates based on Fermi resonance-mixing which is inferred from infrared and Raman spectra.

1. Introduction

With the help of ultrashort laser pulses it has been possible to measure directly the population lifetime of well-defined vibrational modes of polyatomic molecules in the liquid state. For a number of molecules the population decay was found to be of the order of picoseconds [1–4]. Special attention was paid to CH-stretching modes which are of considerable importance for the radiationless decay of electronic excitations.

The investigation of small molecules is facilitated by the small number of normal modes [5]. Frequently we know quite accurately the initially prepared states and have strong indications as to the final states. Recently, it became apparent that mixing by Fermi resonance represents a major coupling mechanism between the initial and the final states, i.e. intramolecular anharmonic coupling between neighboring states of like symmetry is of major importance for the lifetime of the vibrational states [2].

In this paper we present new experimental evidence of the importance of Fermi resonance for the lifetimes of CH-stretching modes. Small changes in the molecular structure can give rise to large changes of Fermi resonance mixing which in turn has a profound effect on the population lifetime. As examples we show data on $CH_2{=}CCl_2$ and trans CHCl=CHCl where only two atoms exchange their positions while the basic structure and the number of atoms are preserved. In addition, we compare the lifetimes of the CH modes of benzene C_6H_6 with the partially deuterated form 1,3,5-$C_6H_3D_3$.

2. Experimental

In our investigations vibrational modes are resonantly excited by ultrashort infrared pulses and the instantaneous degree of population is monitored by spontaneous anti-Stokes Raman scattering of a second probe pulse. Thus two ultrashort light pulses of widely different frequencies are required in our experiments.

The essential features of our experimental system have been described [4]. Briefly, a Nd–glass oscillator amplifier provides single ultrashort laser pulses at 9495 cm^{-1}. These pulses serve as a pump for the parametric generation of infrared pulses tunable between 2800 and 3200 cm^{-1}. The parametric system consists of three $LiNbO_3$ crystals mounted on high-precision turntables. The IR pulses have a duration of 3 ps and $\approx 10^{15}$ quanta per pulse. Probe pulses – at the second-harmonic frequency of the laser pulses, i.e. at 18990 cm^{-1} – monitor the degree of vibrational excitation as a function of time. A large fraction of the generated anti-Stokes photons are collected by placing the specimen at one focus of an ellipsoi-

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dal mirror and focusing the radiation on the entrance slit of a spectrometer of large aperture (spectral resolution $\approx 80\ \mathrm{cm}^{-1}$). The exciting IR pulses and the green probing pulses have perpendicular polarisation. The zero point of the delay time and the time resolution of the system were determined from the cross-correlation curve between IR pulse and probe pulse. To this end the sum frequency of the two incident pulses produced with the help of a properly oriented non-linear $LiNbO_3$ crystal is measured simultaneously as a function of the delay time between the two pulses.

Infrared and Raman spectra of figs. 1 and 3 were taken with standard instrumentation of spectral resolution 4 and $2\ \mathrm{cm}^{-1}$, respectively.

3. Results and discussion

Recent investigations have shown that there is a very rapid exchange of vibrational energy between structurally similar and energetically neighboring vibrational states. For instance, vibrational energy is quickly transferred from the asymmetric to the symmetric CH_2-stretching mode in CH_2Cl_2 or from an infrared active to a Raman active CH-stretching mode in benzene [2,3]. On account of this rapid energy exchange in < 1 ps several vibrational states N are populated in certain molecules during the excitation pulse. When several vibrational states are pumped in the molecule one may observe a longer decay of the reservoir of states.

Theoretical considerations show that the energy transfer between CH-stretching modes of essentially the same energy occurs in a time approximately equal to the dephasing time T_2. If the energy difference $\hbar\omega = \hbar\omega_i - \hbar\omega_f$ is substantial we need a correction factor,

$$T_1(\omega_i \rightarrow \omega_f) = T_2(\omega_i) \exp\left[(\omega/\Omega)^{2/3}\right] , \qquad (1)$$

where Ω is $100\ \mathrm{cm}^{-1}$ We recall that the width of the Raman line gives a lower limit on the pure dephasing time since other broadening processes may contribute to the linewidth.

As pointed out above, the anharmonic coupling, the Fermi resonance, between different but neighboring energy states leads to an intramolecular decay of vibrational energy. For instance, energy flows from the CH-stretching modes via overtones and combination modes to lower-energy states. The degree of 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 [6]. In a recent publication a formula was derived which allows us to estimate the lifetime T_1 of vibrational states [2]:

$$T_1 = N(1+R)^2 R^{-1} \exp\left[(\omega/\Omega)^{2/3}\right] T_2(\mathrm{f}) . \qquad (2)$$

N corresponds to the number of states initially excited. R is a measure of the Fermi resonance, and $T_2(\mathrm{f})$ stands for the dephasing time of the final state. $T_2(\mathrm{f})$ may be estimated from the Raman linewidth $\Delta\nu$ as $T_2(\mathrm{f}) = (2\pi c \Delta\nu)^{-1}$. (It should be noted that $T_2(\mathrm{f})$ is equivalent to $\frac{1}{2}T_2$ measured in coherent Raman scattering.) The energy $\hbar\omega$ represents the difference between the initial and the final state. $\hbar\Omega$ has a value close to $100\ \mathrm{cm}^{-1}$. Difficulties arise for very strong vibrational coupling. The Fermi resonance interaction may become so strong that the theory no longer holds. It should be mentioned that the determination of $T_2(\mathrm{f})$ is difficult in cases of complex spectra. A modified [6] equation (2) may be used where $T_2(\mathrm{i})$, the dephasing time of the initial state, is introduced.

In this paper we present data on four molecules.

3.1. $CH_2{=}CCl_2$

In figs. 1a and 1b we see the symmetric (ν_1) and asymmetric (ν_7) CH_2-stretching vibrations separated by $100\ \mathrm{cm}^{-1}$. The ν_1 mode is excited and its decay is monitored. According to eq. (1) we estimate an energy-transfer time between the two CH-stretching modes of $T_1(\nu_1 \rightarrow \nu_7) \approx 3.3$ ps, where $T_2(\mathrm{f}) \approx 1.2$ ps was taken from the Raman spectrum.

Fig. 1a shows strong Fermi resonance between ν_1 and $\nu_2 + \nu_3$, both of A_1 symmetry, and between ν_7 and $\nu_2 + \nu_6 + \nu_{11}$, both of B_1 symmetry [7]. This observation suggests that we have to consider two decay channels. For the decay $\nu_1 \rightarrow \nu_2 + \nu_3$ we estimate the intensity ratio $R = 0.2 \pm 0.05$ and calculate $T_2(\mathrm{f}) = 0.3$ ps from the Raman linewidth of $\Delta\tilde{\nu} = 17\ \mathrm{cm}^{-1}$. With $N = 1$ and $\omega = 45\ \mathrm{cm}^{-1}$, we calculate from eq. (2) a value of $T_1 = 4 \pm 2$ ps.

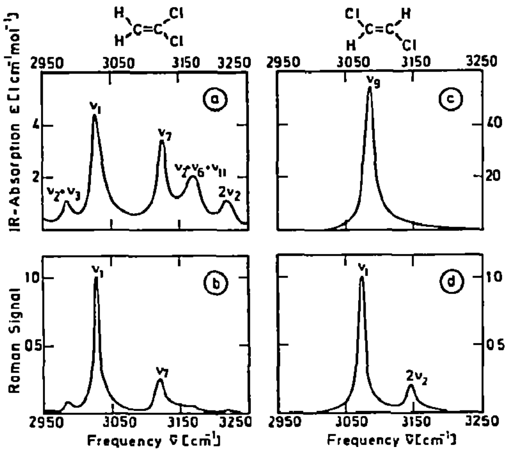

Fig. 1. Infrared absorption (a) and Raman (b) spectra of CH_2CCl_2 between 2950 and 3250 cm^{-1}. Two combination tones are in strong Fermi resonance with the two CH-stretching modes at ν_1 and ν_7. Infrared absorption (c) and Raman (d) spectra of trans-CHClCHCl. There is less Fermi resonance mixing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

For the second decay channel $\nu_7 \to \nu_2 + \nu_6 + \nu_{11}$ we have to take a short dephasing time $T_2(f)$ of the combination tone. We should remember that every component of $\nu_2 + \nu_6 + \nu_{11}$ contributes to the dephasing and, in addition, the low-frequency CH modes undergo faster dephasing than the CH-stretching modes. We estimate $T_2(\nu_2 + \nu_6 + \nu_{11}) \approx 0.2$ ps which is consistent with the observed linewidth. With R = 0.6 ± 0.1, $N = 1$, and $\omega = 45$ cm^{-1} we calculate T_1 = 1.5 ps.

The estimates given above indicate that vibrational energy flows faster out of the ν_7 mode than in the energy transfer $\nu_1 \to \nu_7$. For the interrogated ν_1 mode we simply add the two decay channels $\nu_1 \to \nu_7$ and $\nu_1 \to \nu_2 + \nu_3$ and arrive at a value of $T_1(\nu_1) \approx 2$ ps.

In fig. 2a we present experimental data. 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 ± 1 ps. This experimental finding is in fair agreement with the calculated value for T_1 given above. The broken curves in fig. 2 correspond to the simultaneously measured cross-correlation curves.

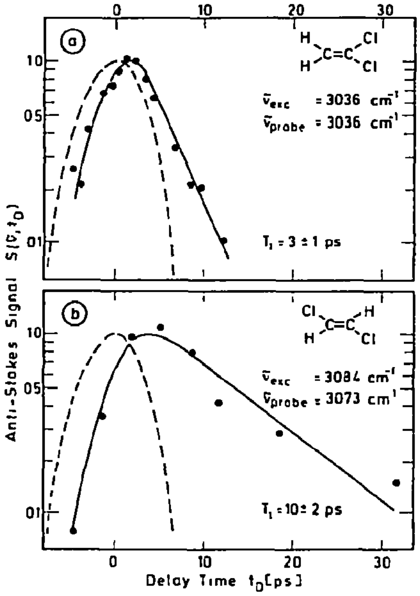

Fig. 2. Anti-Stokes scattering signal versus delay time of the probing pulse. (a) CH_2CCl_2 in CCl_4 (c = 0.35 m.f.). The decay of the CH_2-stretching mode at 3036 cm^{-1} is shown. (b) trans-CHClCHCl in CCl_4 (c = 0.35 m.f.). The CH-stretching mode at 3084 cm^{-1} is excited and the mode at 3073 cm^{-1}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

3.2. *Trans-CHCl=CHCl*

In fig. 1c we see the infrared-active CH-stretching mode ν_9 and in fig. 1d the Raman-active symmetric ν_1 mode. Contrary to CH_2CCl_2 discussed above, we find a considerably smaller Fermi resonance in trans-CHCl=CHCl. The Raman spectrum of fig. 1d suggests some Fermi resonance between ν_1 and $2\nu_2$, both of A_g symmetry [5,7]. With the values R = 0.15 ± 0.02, T_2 = 0.3 ps, $N = 2$, and $\omega = 79$ cm^{-1} we calculate T_1 = 13 ps. It should be noted that there possibly are additional weak Fermi resonances between the ν_9 mode and higher combination modes (eg. $\nu_2 + \nu_5 + \nu_{10}$) buried 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 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. The decay of the signal curve gives 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 lifetime

3.3. C_6H_6

Benzene has been discussed in a recent publication [3]. For clarity and ready comparison we repeat some of the previous results. In fig. 3a the infrared absorption spectrum shows strong Fermi resonance between the ν_{20} fundamental CH-stretching mode and several double and triple combination modes [3,8]. A more detailed inspection of the vibrational energy states of benzene suggests numerous decay channels between the CH-stretching modes and several lower vibrational modes of the molecule It is not surprising, therefore, that we indeed find a very short lifetime of the energy in the CH-stretching modes In fig. 4a the benzene sample was excited via a combination mode at 3090 cm^{-1}. We see the data points in fig. 4a close to the time resolution of the system (the broken curve is the cross-correlation curve) and estimate a decay time of T_1 = 1 ± 0.5 ps.

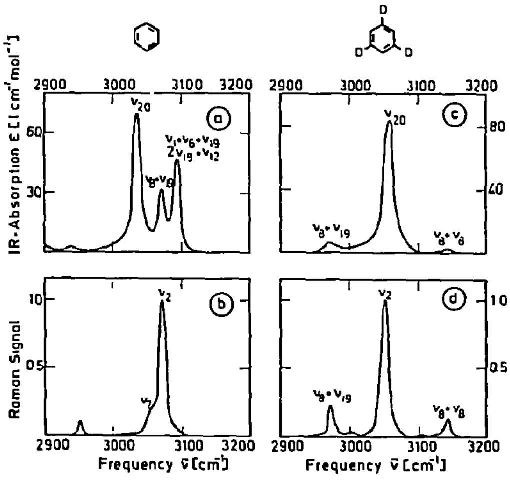

Fig. 3. Infrared absorption (a) and Raman (b) spectra of benzene around 3050 cm^{-1} Note the strong anharmonic interaction with combination modes. Infrared absorption (c) and Raman (d) spectra of 1,3,5-d_3-benzene. The Fermi resonance with combination modes is smaller than in C_6H_6 (a)

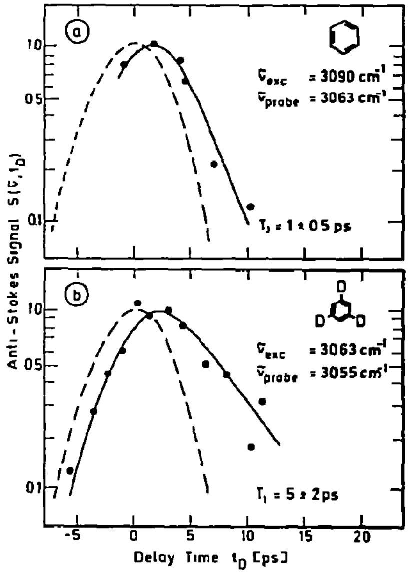

Fig. 4 Anti-Stokes scattering signal versus time. (a) The CH-stretching modes of neat benzene. (b) The CH-stretching modes of neat 1,3,5-d_3-benzene The lifetime of the CH-stretching modes increases upon deuteration.

3.4 1,3,5-$C_6H_3D_3$

The substitution of three hydrogen atoms by three deuterons changes the infrared and Raman spectra substantially. Comparing the infrared spectra of figs. 3a and 3c shows less Fermi resonances in $C_6H_3D_3$. In figs 3c and 3d we see relatively weak anharmonic coupling between the infrared-active mode $\nu_{20}(E')$ and the Raman-active mode $\nu_2(A_1')$ of the CH fundamentals and the combination modes $\nu_8 + \nu_{19}(A_1' + A_2' + E')$ and $\nu_8 + \nu_8(A_1' + A_2' + E')$ [7]. Symmetry arguments allow the interaction of ν_{20} and ν_2 with both combination modes, i.e. we have to consider four decay channels. Adding the different decay rates we finally estimate a lifetime of the CH-stretching modes of 6 ps.

What do we find experimentally for the lifetime for the CH-stretching modes? In fig. 4b we present data on the population and depopulation of the ν_2 mode at 3055 cm^{-1} during and after excitation of the molecule via the infrared-active ν_{20} vibration. The delayed maximum and the slope through the data points suggest a delay time T_1 = 5 ± 2 ps. This value is in good agreement with the estimates made above. It points

Table 1
Summary of energy relaxation times

Molecule	Frequency [a] (cm^{-1})	N	D	T_1 theor (10^{-12} s)	T_1 exp (10^{-12} s)
CH_2CCl_2	3036	1	2	2	3 ± 1
trans-CHClCHCl	3073	2	1	13	10 ± 2
C_6H_6	3063	5	>2	<1	1 ± 0.5
$C_6D_3H_3$	3055	3	4	6	5 ± 2

[a] Frequency of probed CH-stretching modes, N is the number of initially excited fundamental states times multiplicity, D is the number of decay channels considered in the calculation, $T_{1\,\mathrm{theor}}$ is the calculated lifetime, and $T_{1\,\mathrm{exp}}$ is the experimentally determined lifetime.

to the importance of multiple decay channels for vibrational energy.

In table 1 the experimental and calculated lifetimes are summarized for ready comparison.

In the preceding sections we have given arguments that the initially excited CH-stretching modes interact with well-defined overtones or combination modes. The question now arises whether we are able to see the population and depopulation in the subsequent energy states. There are several factors which determine the magnitude of the observable signal. (i) The vibrational mode of interest should have a large Raman scattering cross section; (ii) most of the excited energy should flow into one state, multiple decay channels are unfavorable; (iii) the lifetime of the subsequent state should be equal or larger than the time constant of the primary level. In this way the population in the following state accumulates for ready probing. Inspection of the infrared and Raman spectra in the neighborhood of the subsequent vibrations allows us to estimate anharmonic interaction with other modes. A prediction of the flow of energy to even lower states is thus possible.

As an example we discuss our observations of the molecule $CH_2{=}CCl_2$. We pointed out above that the two CH_2-stretching modes decay via the combination modes $\nu_2 + \nu_3$ and $\nu_2 + \nu_6 + \nu_{11}$. Both combination modes contain the infrared- and Raman-active CH-bending mode at $\nu_2 = 1616$ cm^{-1}. We have searched for the anti-Stokes Raman signal of this bending mode and indeed found evidence for it. The scattered ν_2 signal shifted at 1616 cm^{-1} has a maximum delayed by roughly 1 ps relative to the maximum of the ν_1 curve of fig. 2a and the decay time was approximately equal to the ν_1 data. Our observations suggest a short lifetime of the ν_2 level of $T_1 < 2$ ps. This estimate is quite consistent with the infrared and Raman spectra of the ν_2 mode where strong coupling with a nearby ($\omega \approx 50$ cm^{-1}) overtone $2\nu_9$ is very apparent As an additional decay route one has to consider the coupling to the ν_3 fundamental which is only 220 cm^{-1} from the ν_2 mode.

The results discussed in the preceding paragraph give interesting information on the decay of the ν_2 mode. We do not know, however, whether we probe the combination state or the ν_2 fundamental In the first case, the total vibrational energy of the molecule is ≈ 3000 cm^{-1}, in the second case the total energy is 1616 cm^{-1} and the energy difference is resonantly transferred to neighboring molecules.

4. Conclusions

Our findings show convincingly that the population lifetime of vibrational modes of polyatomic molecules in the liquid phase depends – in a sensitive way – upon the individual vibrational energy states of the whole molecule. Small changes of the symmetry of the molecule or of the frequency of vibrational states may lead to drastic changes of the lifetimes. Fermi resonances observed in infrared and Raman spectra are a valuable guide for an estimate of the population lifetime.

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