Redistribution and Relaxation of Vibrational Excitation of CH-Stretching Modes in 1,1-Dichloroethylene and 1,1,1-Trichloroethane

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Anti-Stokes Raman scattering after resonant infrared excitation with femtosecond light pulses was used to monitor the vibrational excitation of the CH-stretching modes of liquid CH_2CCl_2 and CH_3CCl_3. Selective excitation and probing allowed determination of the various time-constants for the redistribution between the CH-stretching modes and their relaxation. For the symmetric CH-stretching mode of CH_2CCl_2 relaxation times of 3.5 and 9.5 ps are determined for the transfer to overtones and to the asymmetric CH-stretching mode, respectively. For CH_3CCl_3 these time constants are 5.0 and 4.7 ps.

1. Introduction

Ultrafast photochemical reactions on the time scale of 100 fs have been found to be connected with pronounced wave-packet-like modulation of optical signals, indicating the presence of strong vibrational excitation.[1,2] At present there is no detailed understanding of the interconnection between chemical reactions and specific nuclear motions.[3−5] In this context a better knowledge of vibrational excitation, exchange of vibrational energy between specific vibrational modes, and its relaxation out of the molecule is of major interest. In the condensed phase at room temperature the time scale of these processes was found be on the order of 10^{-12} s.[6−10] However, even with the present possibilities of ultrafast technologies, the fast relaxation, the small cross sections, and the related small signal amplitudes impose considerable difficulties for direct observation of the vibrational population. As a consequence most experiments performed in the past had limited sensitivity and spectral or temporal resolution, thus not allowing a direct and complete analysis of fast transfer reactions between "similar" molecular modes.[11]

Recently we presented an experimental system which allows the observation of vibrational population with subpicosecond temporal resolution.[12] In the present paper we will use this setup to study the relaxation of vibrational energy between and out of CH-stretching modes. Of special importance is the possibility of using selective excitation and specific frequency resolved observation of the symmetric and asymmetric CH-stretching modes. Combined with the high temporal resolution of the experiment this feature allows one to follow independently the population changes of the two vibrational modes. This type of experiment yields the complete set of rate constants for energy transfer between and out of the CH-stretching modes which can be compared with simple theoretical approaches.

2. Materials and Methods

The sample molecules 1,1-dichloroethylene and 1,1,1-trichloroethane were obtained from Merck No. 803209 (1,1-dichloroethylene) and No. 108749 (1,1,1-trichloroethane) at purities of >99% and >99.5%, respectively. The sample was dissolved in CCl_4 (Merck No. 102209) at concentrations of 1:1 (1,1-dichloroethylene) and 1:2 (1,1,1-trichloroethane) v/v. In the time-resolved measurements the sample volume was exchanged between two subsequent excitation processes in order to prevent heating of the sample.

Stationary characterization was performed as follows: The spontaneous Raman spectra were recorded with a similar experimental setup as used in the transient experiment (see below) with some modifications: 5 mW of the 488-nm line of an Ar^+ laser was used as laser source and the spectrometer was equipped with a 1800 groves/mm grating to achieve a higher spectral resolution (<1.5 cm^{-1}). The Raman scattered light was detected in the backward direction (180° excitation-detection geometry). The solid lines in Figures 1a and 2a show the spectrum recorded with parallel polarization of laser and detection; the broken curve was recorded with crossed polarization. The infrared spectra were measured with a Bruker IFS-66 FTIR spectrometer set to a spectral resolution of 4 cm^{-1}.

The experimental system for the time-resolved experiments has been previously described in detail.[12] Here only the important features for the present experiment are given: Vibrational relaxation is measured in an excite-and-probe experiment with subpicosecond light pulses. Tunable infrared pulses are used to excite specific vibrational modes while anti-Stokes Raman scattering of a delayed probing pulse at 815 nm monitors the vibrational excitation.[11] The experiment was operated at a repetition rate of 1000 Hz. The IR pulses had a spectral width of 100 cm^{-1}, a duration of 120 fs, and an energy of ≈2 μJ. They were focused at a beam diameter of 100 μm. The probing "laser" pulses were adjusted to have a spectral width of 45 cm^{-1}. By this method a width of the instrumental response function of 700 fs was obtained which was determined by the duration of spectrally narrow probing pulses. To reduce artifacts due to rotational depolarization, pump and probe pulses had a relative polarization of 65°.[13−15] In the experiments the anti-Stokes signal was recorded over three runs of the delay line with an averaging time for each setting of the delay line of 120 s. The signal background, recorded before excitation, i.e., at delay times ≈−2 ps, was subtracted. The disturbing signal spikes by sphaerics (cosmic rays hitting the sensitive area of the CCD detector),

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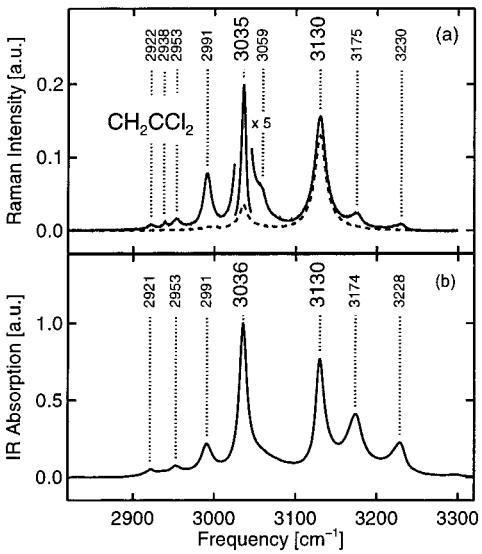

Figure 1. Raman (a) and infrared spectrum (b) of 1,1-dichloroethylene in the region of the CH-stretching modes. The Raman spectrum was recorded with parallel (solid line) and perpendicular (broken line) polarization of laser and detection. It shows fundamentals at 3035 cm^{-1} (ν_1) and 3130 cm^{-1} (ν_7). It is interesting to note that all bands besides the anti-symmetric CH-stretching vibration ν_7 are polarized.

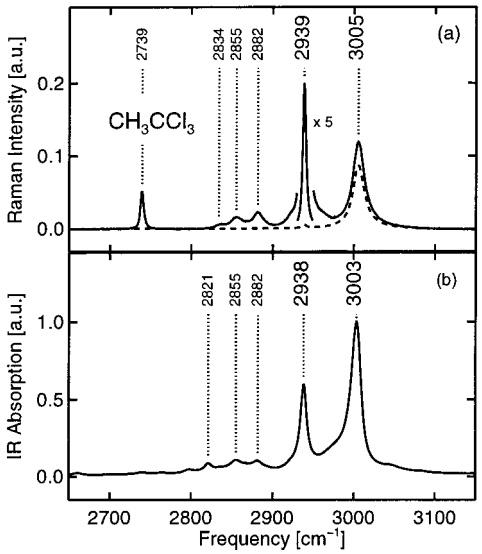

Figure 2. Raman (a) and infrared spectrum (b) of 1,1,1-trichloroethane in the region of the CH-stretching modes. The Raman spectrum was recorded with parallel (solid line) and perpendicular (broken line) polarization of laser and detection. It shows the fundamentals at 2939 cm^{-1} (ν_1) and 3005 cm^{-1} (ν_7).

visible at large averaging times, were removed. The anti-Stokes energy is a direct measure of the vibrational excitation of the observed mode. To compare the relative population of the two modes one has to scale the signals by their respective Raman cross sections.

The analysis of the experimental data was performed with the rate equation system shown in Figure 6, where the different CH-stretching modes are considered explicitly. Irreversible decay of the population out of these modes (ν_1 and ν_7 in our case) is assumed to occur via microscopic rates γ_{01} and γ_{07}. The transfer between these modes was described by the rates γ_{71} and γ_{17}. When a state is degenerate (such as ν_7 in 1,1,1-trichloroethane) it was treated in the reaction model as a pair of states with fast internal population transfer. Within this model the experimentally detectable population changes are described

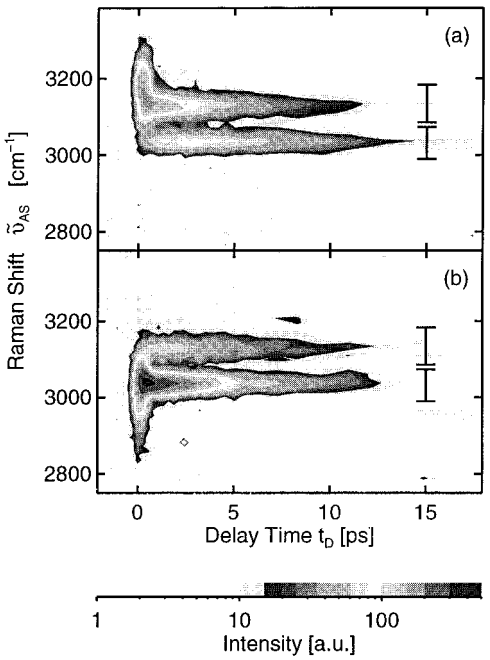

Figure 3. Anti-Stokes Raman signal of 1,1-dichloroethylene plotted as function of Raman shift and delay time. At $t_D = 0$ a short excitation laser pulse centered at 3140 cm^{-1} (a) and 3020 cm^{-1} (b) was applied to the sample. At later times the Raman signal of the two CH-stretching modes can clearly be separated. The decay of the individual modes can be clearly observed. The bars indicate the spectral range used when displaying the integrated intensities in Figure 4.

by the sum of exponentials, where the time constants are related to the eigenvalues of the matrix of microscopic rates γ_{ij}. Since different starting populations of ν_1 and ν_7 can be achieved by tuning the excitation wavelength, mode selective observation yields enough information (namely, the two eigenvalues $1/\tau_i$ and the relative populations) to deduce the microscopic rates of the reaction model.

For data handling the experimental points were integrated over the bandwidth of 95 cm^{-1} (1,1-dichloroethylene) and 70 cm^{-1} (1,1,1-trichloroethane). The data were fitted by a model function consisting of two exponentials convolved by the instrumental response function. The contribution of a fast decaying signal from overtones, combination bands, or optical nonlinearities is considered via an additional term proportional to the instrumental response function. The initial populations of the CH-stretching modes in the experiments are determined by extrapolating the exponential functions back to $\tau_D = 0$.

3. Vibrational Spectra

1,1-Dichloroethylene. CH_2CCl_2 has two CH-stretching modes which are both Raman and IR active. The antisymmetric CH-stretching mode ν_7 is at 3130 cm^{-1}, the symmetric ν_1 mode at 3035 cm^{-1}. Of special interest for the relaxation of vibrational energy out of the CH-stretching modes are overtone and combination modes anharmonically coupled to the fundamentals.[16] The Raman spectrum, Figure 1a, displays such bands at 2922, 2938, 2953, 2991, 3059, 3175, and 3230 cm^{-1}. These bands obtain their intensities via Fermi resonance from the symmetric ν_1 mode. This connection can be deduced from the observation that these bands are strongly polarized (see solid and broken curve in Figure 1a) and thus belong to the A_1 symmetry type. Some of these bands also show up in the IR spectrum of Figure 1b. An assignment of the different bands has been given in refs 17 and 18.

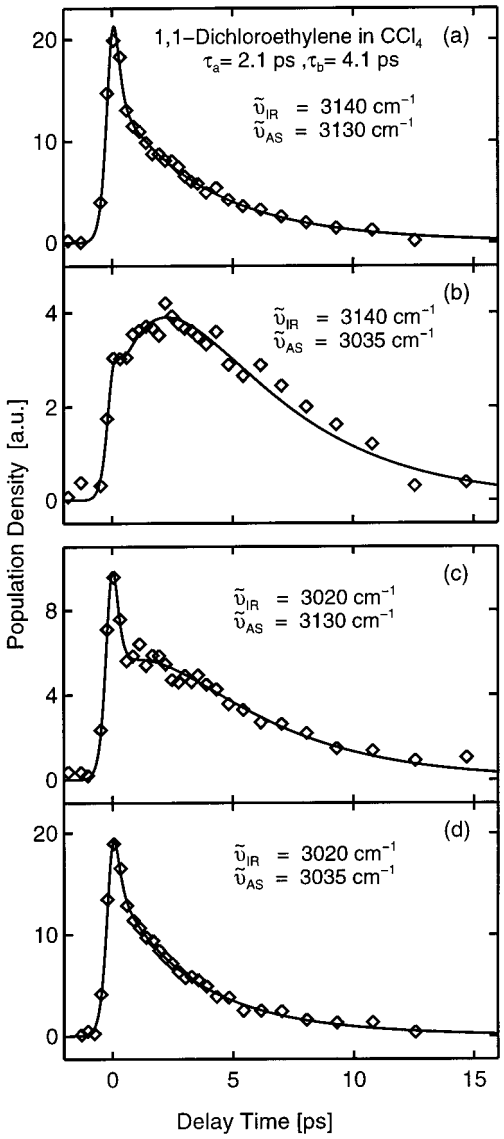

Figure 4. Vibrational population after excitation of the antisymmetric (a, b) and the symmetric (c, d) CH-stretching vibration of 1,1-dichoroethylene at time $t_D = 0$. The data points (diamonds) are obtained by spectral integration over the Raman bands (see Figure 3) and scaling by their respective Raman cross sections. The solid line shows a biexponential fit with the time constants 2.1 and 4.1 ps. In the model curve a contribution of the instrumental response function was added in order to account for nonlinear processes found at time zero.

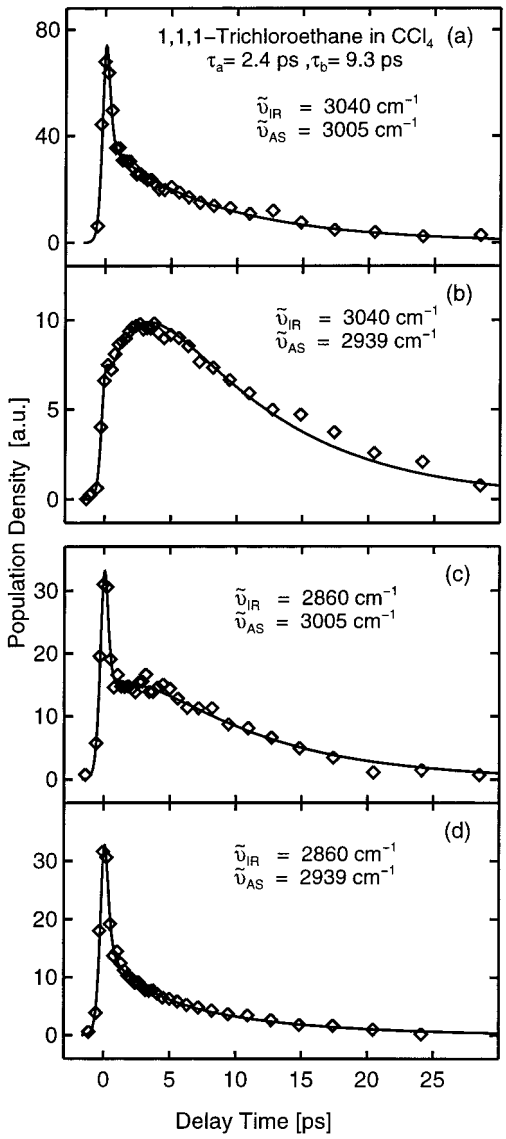

Figure 5. Vibrational population after excitation of the degenerate (a, b) and the symmetric (c, d) CH-stretching vibration of 1,1,1-trichoroethane at time $t_D = 0$. The data points (diamonds) are obtained by spectral integration over the Raman bands (integration range: 70 cm^{-1}) and scaling by their respective Raman cross sections. The solid line shows a biexponential fit with the time constants 2.4 and 9.3 ps. In the model curve a contribution of the instrumental response function was added in order to account for nonlinear processes found at time zero.

1,1,1-Trichloroethane. In 1,1,1-trichloroethane (see Figure 2) the two CH-stretching modes are also Raman and IR active. The asymmetric CH-stretching mode ν_7 at 3005 cm^{-1} is degenerate. The symmetric CH-stretching mode is found at 2939 cm^{-1}. Again the Raman and IR spectra display a number of overtone and combination bands in the range between 2700 and 3350 cm^{-1}. Most important for relaxation out of the CH-stretching modes seem to be the bands at 2739, 2834, 2855, and 2882 cm^{-1} which are well seen in the Raman spectrum. Due to the polarization of the Raman spectra, one can state that these modes are coupled to the symmetric CH-stretching vibration ν_1. Detailed assignments of these modes have been given in the literature.[19,20]

In both samples, the large spectral width of the exciting IR pulses (≈100 cm^{-1}) prevents the excitation of a single vibrational transition. To generate starting populations with strong differences in the population of the symmetric and antisymmetric CH-stretching modes, the spectral position of the IR pulses is shifted to the red or the blue wing of the CH-stretching region. In this way we obtain a predominant population of one of the fundamentals. However, there is always an additional excitation of overtone and combination bands. This can lead to fast initial transients in the Raman signal. In the qualitative analysis of

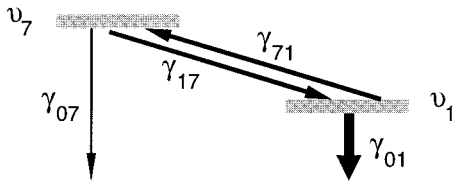

Figure 6. Reaction model for the vibrational energy transfer between and out of the CH-stretching modes. The amplitudes and time constants from the biexponential fit of the experimental data and the principle of detailed balance were used to obtain the microscopic reaction rates γ_{ij} presented in Table 1.

the experimental data we considered this contribution by fitting it with the instrumental response function (see above).

4. Time-Resolved Observations

4.1. 1,1-Dichloroethylene. A gray scale plot of the anti-Stokes Raman signal vs delay time is shown in Figure 3 for the two different excitation wavelengths used. At delay time zero the signal is concentrated around the anti-Stokes frequency related to the spectrum of the exciting IR pulse (3140 cm^{-1}, Figure 3a, and 3020 cm^{-1}, Figure 3b). This interesting feature may be caused by the driving of the vibrations (fundamentals and overtones) with the IR pulse or due to a nonlinear background.[21] At later delay times the individual signals from the two CH-stretching modes can be well followed. For the initially excited mode we see a continuous decay, while for the other mode a delayed rise of the signal can be observed. Figure 4 displays the time-dependence of the anti-Stokes signal for the two bands obtained by integrating over the spectral range indicated by the bars in Figure 3. Figure 4a,b represents results for the high-frequency excitation case: For the initially excited anti-Stokes CH-stretching mode one finds—after the rapid decay of the signal due to the instantaneous sample response —a decrease which extends over more than 10 ps (Figure 4a). For the symmetric CH-stretching mode (Figure 4b) the instantaneous part of the signal is followed by a signal rise before the signal starts to decay after $t_D = 3$ ps. When the low-frequency excitation in the symmetric CH-stretching mode is used (Figure 4c,d) one observes well the decay of the signal for both modes at later delay times. A delayed rise of the signal is not evident for the accepting high frequency mode where one only observes a plateau at early delay times (Figure 4c). The results from a modeling of these data yield a detailed description of the reaction processes: After the instantaneous response the data points of all four curves are fitted well by biexponential functions with the time constant $\tau_a = 2.1 \pm 0.3$ ps and $\tau_b = 4.1$ ps $\pm$ 0.6 ps. The choice of the same two time constants for all four signal traces is a consequence of the reaction model with two vibrational states.

4.2. 1,1,1-Trichlorethane. In Figure 5 the observations on CH_3CCl_3 are shown for the two IR excitation pulses centered at 3040 cm^{-1} (Figure 5a,b) and 2860 cm^{-1} (Figure 5c,d). Qualitatively the anti-Stokes signals of the degenerate asymmetric ($\nu_{AS} \approx 3005$ cm^{-1}) and the symmetric CH-stretching mode ($\nu_{AS} = 2939$ cm^{-1}) behave in a similar way to the ones observed for 1,1-dichloroethylene. A fast instantaneous response due to driven modes and nonlinear coupling is followed by a biexponential decay for the two situations where excitation and probing is done on the same mode (Figure 5a,d). In the case of an initial excitation transfer to the observed mode (Figure 5b,c), the rise with τ_a precedes the slower decay with τ_b. In CH_3CCl_3 the two time constants are found to be $\tau_a = 2.4 \pm 0.3$ ps and $\tau_b = 9.3 \pm 1$ ps.

5. Discussion

Qualitatively the experimental observations can be summarized as follows:

When excitation and probing is on the same mode, one observes a continuous decay of the signal, which is biexponential.

When excitation is at a higher frequency than probing, the population shows first a rise and a subsequent decay.

The population changes can be modeled for both molecules by two time constants.

TABLE 1: Time Constants for Relaxation and Redistribution

	time constants, ps			
	relaxation of		redistribution of	
	symmetric mode $1/\gamma_{01}$	asymmetric mode $1/\gamma_{07}$	asymmetric to symmetric mode $1/\gamma_{17}$	symmetric to asymmetric mode $1/\gamma_{71}$
CH_2CCl_2	3.5	8.6	5.9	9.5
CH_3CCl_3	5.0	16.2	6.7	4.7

TABLE 2

ω_j	R_j	T_{2j}, ps	$1/\Gamma_{j1}$, ps
	a		
2922	0.0047	0.74	471.3
2938	0.0047	1.04	599.0
2953	0.019	0.56	74.5
2991	0.11	0.53	10.3
3059	0.079	0.37	8.0
3175	0.051	0.27	20.6
3230	0.0093	0.45	231.6
	b		
2739	0.050	1.21	131.2
2834	0.015	0.53	99.3
2855	0.062	0.25	11.2
2882	0.050	0.45	19.7

For the analysis of the experimental data we used the level scheme of Figure 6, where the two fundamentals are considered explicitly. Relaxation out of these two modes with γ_{07} and γ_{01} is assumed to be an irreversible process. This is justified if a potential back transfer (which should have a rate in the order of γ_{07} and γ_{01}) from the accepting modes (overtones and combinations) is much slower than their decay rates γ_j. If we take the spectral widths $\Delta\nu_j$ or the dephasing times T_{2j} of the accepting modes as a measure of their decay rates $\gamma_j \leq 2\pi\Delta\nu_j$, the analysis yields a consistent picture with $\gamma_j \gg \gamma_{07}$ and γ_{01}. For the ratio of the internal rates connecting asymmetric and symmetric CH-stretching modes we assume that the principle of detailed balance holds: $\gamma_{71} = \gamma_{17} g_7 \exp(-\Delta E_{17}/k_B T)$. Where g_7 is the degeneracy of state υ_7 and ΔE_{17} is the energy difference $\Delta E_{17} = E_7 - E_1$.

For both molecules the experimental data (amplitudes related with the various rates and the rates themselves) can be used to invert the rate equation system and determine the microscopic rates of the reaction model (see Table 1). In both molecules the fastest relaxation out of the CH-stretching modes occurs from the symmetric ν_1 vibration. This relaxation channel has a time constant $1/\gamma_{01} = 3.5$ ps and $1/\gamma_{01} = 5$ ps for CH_2CCl_2 and CH_3CCl_3, respectively. This observation is supported by the qualitative model of Fischer et al.,[16,22] where the vibrational energy relaxation should proceed via anharmonic coupling to overtones and combination bands of appropriate symmetry. We focus our discussion here on the relaxation out of the symmetric CH-stretching modes, where we can deduce the anharmonic coupling from the Raman intensities of the accepting modes of the same symmetry (see Figures 1a and 2a).[23] In Table 2 we present the time constants for the different relaxation channels calculated by using the formula given in ref 16.

$$\Gamma_{j1} = \frac{R_j}{(1+R_j)^2} \exp\left[-\left(\frac{|\omega_j - \omega_1|}{\Omega}\right)^{2/3}\right] \frac{1}{T_{2j}} \qquad (1)$$

with the frequencies ω_j and the dephasing times T_{2j}. R_j describes the anharmonic coupling deduced from the Raman intensities I_j of the modes: $R_j = I_j/I_1$. Ω is related to the interaction length

and the effective collision mass.[16] For small molecules and small energy transfer, $\hbar|\omega_j - \omega_1| \leq k_B T$, Ω is close to 100 cm^{-1}.[16] The intensities, frequencies, and dephasing times are deduced from the spontaneous Raman spectra of Figures 1a and 2a by a fit using Lorenzian functions. The total relaxation rate out of the ν_1 modes is obtained by summing over all relaxation channels $\gamma_{01} = \sum_j \Gamma_{j1}$. For CH_2CCl_2 and CH_3CCl_3 we obtain values of 3.4 and 6.3 ps, close to the experimental values of 3.5 and 5 ps, respectively (see Table 1). Considering the qualitative nature of eq 1 and uncertainties of finding all relaxation channels, this is a surprisingly good agreement.

In CH_3CCl_3 the energy transfer between the CH-stretching modes, i.e., from the symmetric to the 2-fold degenerate asymmetric CH-stretching mode, takes $1/\gamma_{71} = 4.7$ ps. This is equivalent with a rate $\gamma = (9.4\ ps)^{-1}$ for each individual relaxation channel. For CH_2CCl_2 (where the accepting mode is nondegenerate) one finds $1/\gamma_{71} = 9.5$ ps. It is interesting to note that this energy relaxation between two neighboring modes, where the same atoms are involved with very similar motions, is of the same order as or even slower than the relaxation out of the symmetric CH-stretching mode to overtones of completely different nuclear motion. In a simplified picture one may argue that the exchange between the two CH-stretching modes should be related to the dephasing time T_2. Since the difference in nuclear motion between asymmetric and symmetric CH-stretching modes is mostly a phase difference of the motion of one H-atom by 180°, single dephasing collisions could induce such a phase jump and with that the relaxation from one CH-stretching mode to the other. Thus the energy exchange should occur on the time scale of the dephasing process. From the spectral width of the Raman spectra the dephasing times $T_2 = 1/(\pi\Delta\nu)$ can be deduced. Since T_2 is conventionally defined to describe the decay of the vibrational amplitude, it has to be divided by two in order to account for intensity or population decays.[21] The relevant values are $T_2/2 = 0.8$ ps and $T_2/2 = 1.1$ ps for the symmetric CH-stretching modes of CH_2CCl_2 and CH_3CCl_3, respectively. The considerably longer duration of the transfer time $1/\gamma_{71}$ suggests that if the above-mentioned collision model applies, only very few of all phase-disturbing collisions are able to change the nuclear motion in such a way that a CH-stretching motion is converted to an antisymmetric one.

In conclusion, we have presented experimental results on fast vibrational relaxation between and out of different CH-stretching modes in liquids. We have shown that the excitation exchange occurs on the 5−10 ps time scale. In 1,1-dichloroethylene and 1,1,1-trichloroethane the dominant relaxation channel out of the CH-stretching modes is via the symmetric vibration. Here several efficient reaction channels exist to close-lying overtone and combination bands of the same symmetry. For the asymmetric CH stretching mode where no accepting modes of appropriate symmetry were seen in the Raman spectra the relaxation is much slower. As a consequence the symmetry of the involved modes seems to be of dominant importance for the energy transfer process.

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