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Ultrafast vibrational dynamics of small organic molecules in solution

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In this paper we present a time-resolved study of the vibrational relaxation after excitation of the asymmetric CH_2 stretch vibration of dibromomethane and diiodomethane and the C–H stretch vibration of 1,1,2,2-tetrabromoethane. The experiments were performed in a polar and a nonpolar solvent in order to study the influence of the polarity of the solvent on the relaxation. We observe that in both types of solvent the vibrational energy transfer is successively intra- and intermolecular and that the intramolecular relaxation leads to a shift of the transition frequency of the excited molecular vibration. We discuss the experimentally determined time constants of the relaxation in terms of the energy differences between the molecular vibrations and the interactions with the solvent.

INTRODUCTION

In the past many time-resolved studies have been performed on the energy relaxation of excited molecular vibrations in the condensed phase.^{1–20} In all of these studies a time constant for the relaxation was determined, but very little information on the nature of the relaxation channels could be obtained. These last studies show that an excited vibration with a relatively high energy relaxes preferentially via an energy transfer to combinations of other vibrations within the molecule. The rate at which such a relaxation process takes place depends on the density of vibrational states at the energy of the excited vibration and the anharmonic coupling with combination tones of approximately equal energy. In small molecules with a limited number of molecular vibrations, the magnitude of the energy gap with a few strongly coupling combination tones can be the most important factor that determines the relaxation rate.

In a liquid, the rate of energy transfer is strongly influenced by the interactions with the surrounding molecules. During inelastic binary collisions the excess energy of the excited vibration with respect to the coupling combination tones can be transferred to rotational or translational degrees of freedom,^{21,22} thus making the energy transfer possible.

In this paper we study the vibrational dynamics of the small organic molecules dibromomethane (CH_2Br_2), diiodomethane (CH_2I_2), and 1,1,2,2-tetrabromoethane ($\text{C}_2\text{H}_2\text{Br}_4$) in a polar (CD_3COCD_3) and a nonpolar (CCl_4) solvent.

By comparing the results on CH_2Br_2 and CH_2I_2 with those on 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$, we can investigate how the relaxation changes when the two hydrogen atoms are bonded to different carbon atoms. By performing the experiments with CCl_4 and CD_3COCD_3 as solvent, we investigate the influence of the polarity of the solvent on the relaxation.

EXPERIMENTAL

The experiments are performed using infrared saturation spectroscopy. In this technique a significant fraction of the molecules in the sample is excited with an intense infrared pulse (pump). This leads to a bleaching of the sample if the molecular vibration has an anharmonic progression.

The time dependence of the bleaching and thus of the excitation can be monitored by measuring the transmission of a weak infrared pulse (probe) as a function of the delay with respect to the pump.⁴

The infrared pulses that we use in our experiment are generated via parametric generation and amplification in LiNbO_3 crystals.^{20,23} The crystals are pumped with the output of a passively and actively mode-locked Nd:YAG laser (energy: 40 mJ, pulse duration: 35 ps, wavelength: 1064 nm, repetition rate: 10 Hz). The experimental setup is described in detail in Ref. 20. This setup generates intense infrared pulses that are tunable from 2200 to 7200 cm^{-1} . The pulse duration of these pulses is approximately 20 ps and a pulse at 3000 cm^{-1} has a typical energy of 200 μJ . The bandwidth of the pulses at this wave number is approximately 15 cm^{-1} which implies that the pulses are not bandwidth limited.

We perform the experiment with a pump–probe setup. A small part of an intense infrared pulse is reflected by a thin CaF_2 plate and sent into a variable delay. This part of the pulse serves as the probe and is focused into the sample by a CaF_2 lens with a focal length of 5 cm, together with the strong part (pump) that was transmitted by the thin CaF_2 plate. Each experimental point is an average over hundreds of laser shots.

The experiments are performed with solutions of 0.1 M CH_2Br_2 and CH_2I_2 and 0.05 M 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ in CCl_4 and CD_3COCD_3 . We measured ir spectra of all samples with a double-beam Perkin and Elmer 881 spectrometer in order to check the optical density and to determine the maximum and the shape of the absorption band.

RESULTS

We performed an extensive study of the wavelength dependence of the transmission of the probe by tuning the central frequency of the laser pulses through the whole absorption band of the asymmetric CH_2 stretch vibration of CH_2Br_2 and CH_2I_2 and the C–H stretch vibration of 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$. Typical results are presented in Figs. 1–6. In the top figures (a), the central frequency of the laser pulses is higher than the maximum of the absorption band, whereas in the bottom figures (b), the central frequency is lower than the maximum of the absorption band. In all fig-

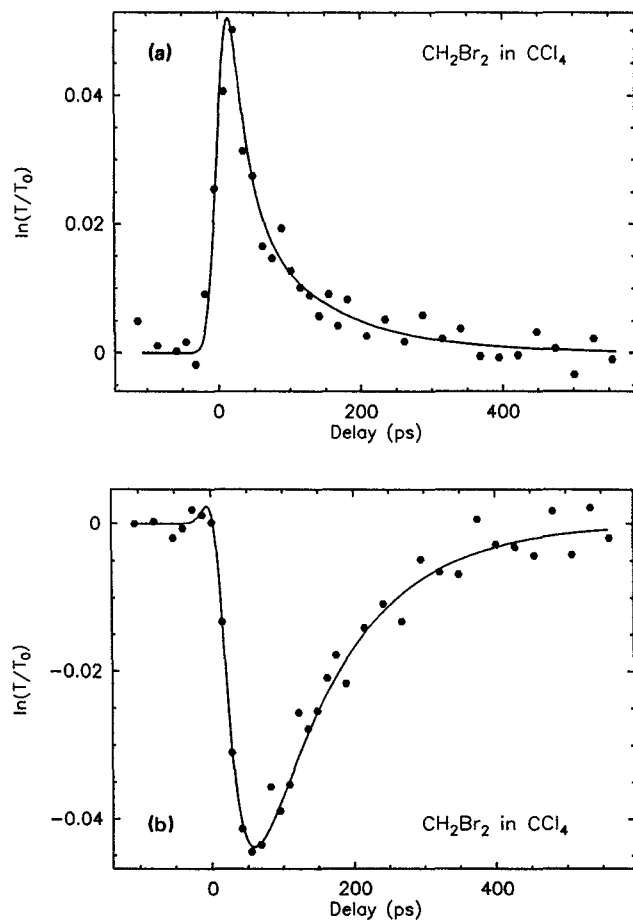


FIG. 1. Relative transmission ($\ln[T/T_0]$) of an infrared probe pulse as a function of the delay between probe and pump pulse for the asymmetric CH_2 stretch vibration of CH_2Br_2 dissolved in CCl_4 ($\nu_{\text{max}} = 3062 \text{ cm}^{-1}$) for two different central frequencies. Pump and probe have the same frequency spectrum. The numerical results that are calculated with the time constants of Table I are represented by the solid curves. (a) 3064 cm^{-1} , (b) 3052 cm^{-1} .

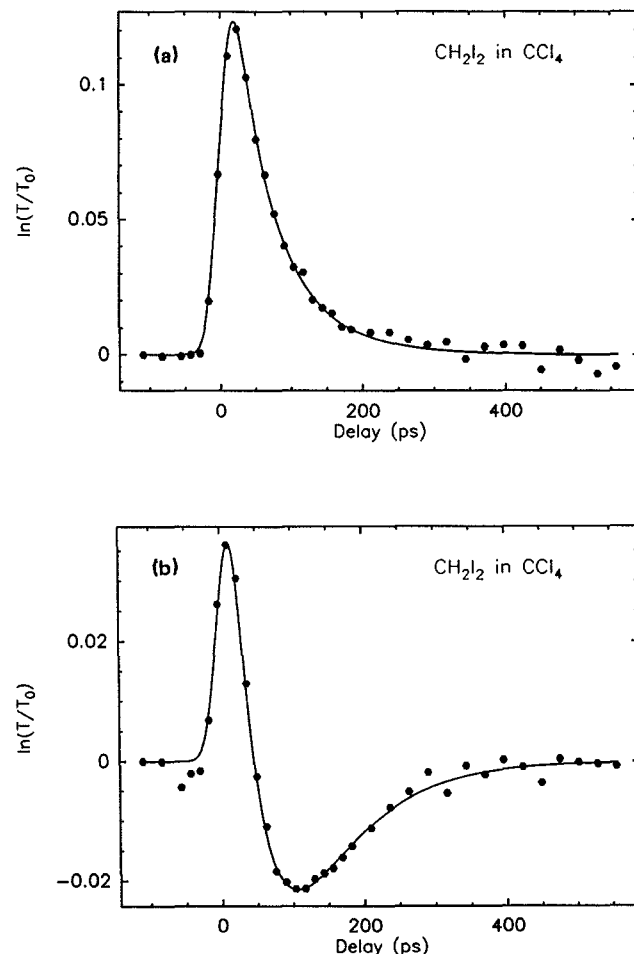


FIG. 2. As Fig. 1 for the asymmetric CH_2 stretch vibration of CH_2I_2 dissolved in CCl_4 ($\nu_{\text{max}} = 3065 \text{ cm}^{-1}$). (a) 3066 cm^{-1} , (b) 3054 cm^{-1} .

ures except for Figs. 1(b), 3(b), and 4(b), the transmission of the probe is increased when pump and probe overlap due to the bleaching of the sample by the pump. This increase is followed by a decrease due to the relaxation of the excited vibrations.

When the central frequency of the laser pulses is lower than the maximum of the absorption band, we observe for all samples an overshoot of the decrease in transmission of the probe. This overshoot indicates that during the relaxation the absorption band of the excited vibration shifts to a lower value and better into resonance with the spectrum of the probe. The overshoot can not be due to excitation of the first overtone of the excited vibrations, because this excitation requires a frequency that is $100\text{--}200 \text{ cm}^{-1}$ lower.

We deduce from these results that the relaxation takes place via two consecutive relaxation processes. In a first relaxation process, a significant amount of the energy of the asymmetric CH_2 stretch vibration of CH_2Br_2 and CH_2I_2 and the energy of the C-H stretch vibration of 1,1,2,2-

$\text{C}_2\text{H}_2\text{Br}_4$ is transferred to other vibrations with lower energies within the molecule. This energy transfer leads to a shift of the transition frequency to a lower value due to anharmonic coupling of the molecular vibrations. Although this first process is not necessarily purely intramolecular, we will refer to it in the following as intramolecular vibrational relaxation (IVR). After this relaxation process, the energy of these other vibrations in the molecule is transferred to the solvent or to vibrations within the molecule that do not influence the absorption band. Due to this relaxation process the absorption band shifts back to its original value. This type of vibrational relaxation has been observed previously after excitation of the C-H stretch vibration of CHCl_3 , CHBr_3 ,^{13,16,19} and CHI_3 .²⁰

We have studied the temperature dependence of the absorption band with a conventional ir spectrometer (Perkin and Elmer 881). We observed that with CCl_4 as solvent the absorption bands of the asymmetric CH_2 stretch vibration of CH_2Br_2 and CH_2I_2 and the C-H stretch vibration of 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ hardly depend on temperature. With CD_3COCD_3 as solvent an increase in temperature leads to a steepening of the low-frequency side of all three absorption bands. In the time-resolved experiments we observe that

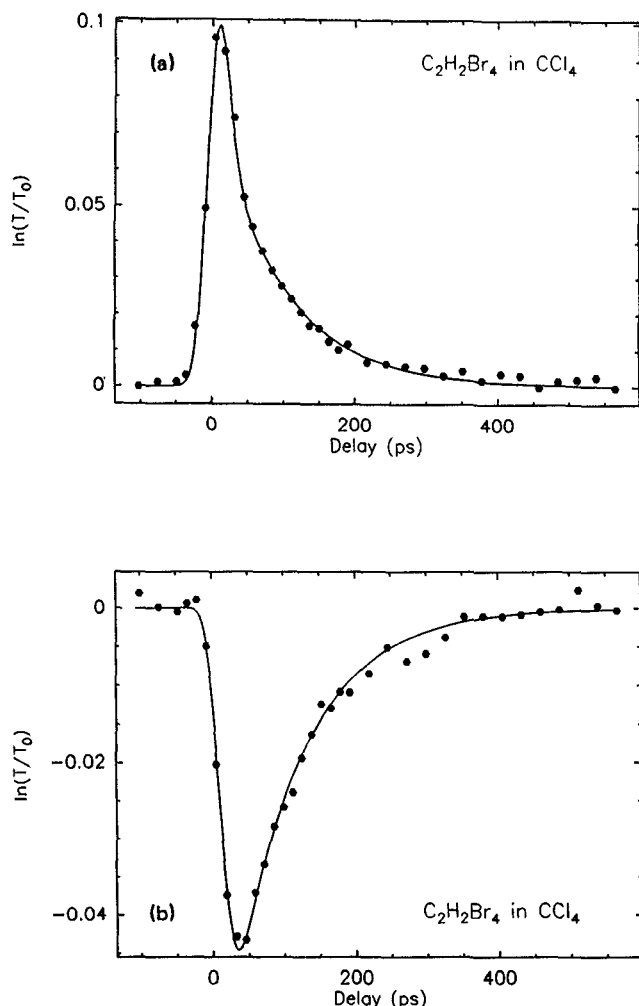


FIG. 3. As Fig. 1 for the C-H stretch vibration of 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ dissolved in CCl_4 ($\nu_{\text{max}} = 2993 \text{ cm}^{-1}$). (a) 2998 cm^{-1} , (b) 2985 cm^{-1} .

with CCl_4 as solvent the transmission of the probe returns to its initial value for large delays. With CD_3COCD_3 as solvent we observe that when the central frequency of the laser pulses is initially below the maximum of the absorption band, the transmission of the probe remains at an increased level for large delays. From the comparison of the temperature dependence of the absorption bands and the change in absorption coefficient for large delay times [Figs. 4(b), 5(b), and 6(b)], we deduce that in the second relaxation process the energy is equilibrated over all degrees of freedom, leading to a rise of the local temperature of $20 \pm 5 \text{ K}$. This implies that a large part of the energy is transferred to the solvent. Therefore, we will refer to this second relaxation process in the following as an intermolecular energy transfer (IET), although there will still be some energy stored in low-frequency modes of the initially excited molecule.

With this model we can also explain the transmission of the probe as a function of the delay when the central frequency of the laser pulses is higher than the maximum of the absorption band. In this case the transition shifts out of the bandwidth of the laser pulses after the IVR process and the transmission of the probe remains increased as long as the molecules have not relaxed via the IET process.

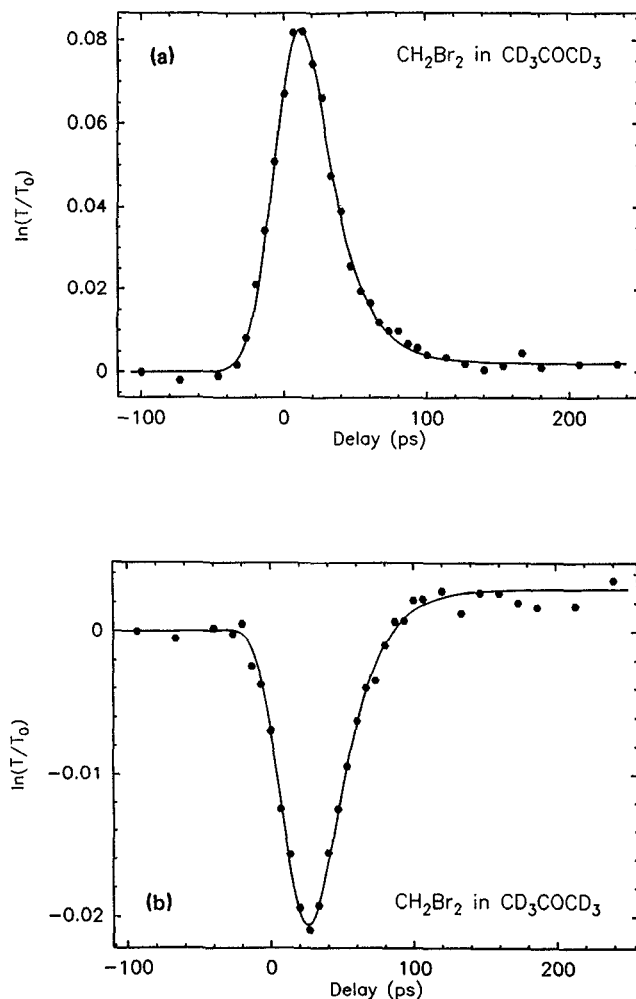


FIG. 4. As Fig. 1 for the asymmetric CH_2 stretch vibration of CH_2Br_2 dissolved in CD_3COCD_3 ($\nu_{\text{max}} = 3077 \text{ cm}^{-1}$). (a) 3079 cm^{-1} , (b) 3053 cm^{-1} .

The experimentally observed increases and decreases of the transmission of the probe are not only determined by the central frequency of the laser pulses and the shift of the absorption band after the IVR process, but also by the values of the relaxation time constants of the IVR and the IET process. The relative rate of the IVR process compared to the IET process is very important for the transmission of the probe. If the IVR is fast, there will be many molecules in the sample for which the transition frequency is shifted. If the IVR process is also fast, compared to the pulse duration, we do not observe any increase in transmission when the vibration is excited sufficiently below the maximum of the absorption band [Figs. 1(b), 3(b), and 4(b)]

The time constants of the two relaxation processes can be determined by comparing the experimental results with numerical calculations based on a rate-equation model. The calculations use as input the pulse parameters of pump and probe, and as fit parameters the absorption coefficients and the exponential time constants of the relaxation. The calculated transmission curves of the probe are represented in Figs. 1–6 by the solid curves. The resulting time constants are presented in Table I. It should be noted that even in the

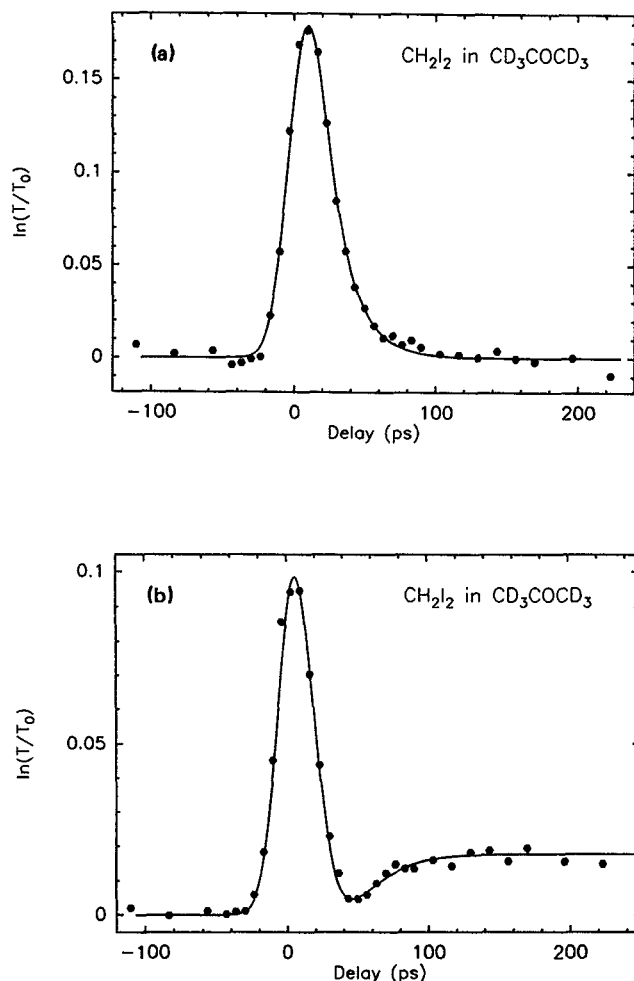


FIG. 5. As Fig. 1 for the asymmetric CH_2 stretch vibration of CH_2I_2 dissolved in CD_3COCD_3 ($\nu_{\text{max}} = 3067 \text{ cm}^{-1}$). (a) 3067 cm^{-1} , (b) 3061 cm^{-1} .

case where the IVR process is very fast (Figs. 3–6), it is still possible to determine the time constant of this process accurately from the delay between the minimum of the transmission of the probe and the point of best overlap between pump and probe.

The absorption coefficient is a function of the spectral profiles of the pulses and the absorption band and of the detuning from the maximum of the absorption band. Under the assumption that the shape and amplitude of the absorption band do not change after the IVR process, we can use the absorption coefficients from the numerical simulations to determine the shift of the absorption band after the IVR process. Because the spectral profile of the absorption band is asymmetric, we model it with two half-Gaussians of different widths. The resulting shifts of the absorption band are presented in Table II.

DISCUSSION

In a previous study on CH_2Br_2 and CH_2I_2 dissolved in CCl_4 ,⁶ the time constants of the relaxation of the symmetric CH_2 stretch vibration were determined by measuring the spontaneous anti-Stokes–Raman signal as a function of the

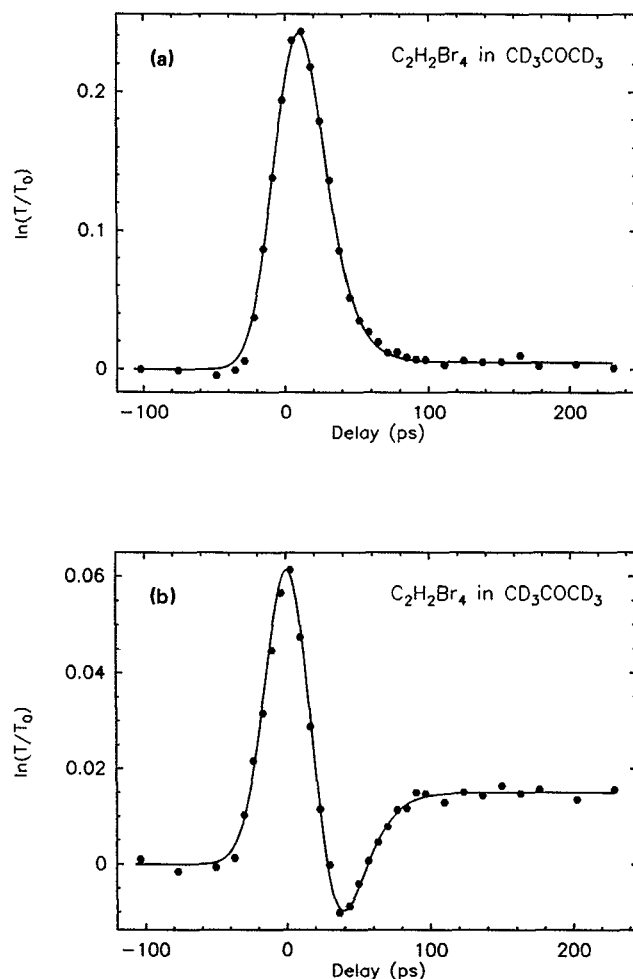


FIG. 6. As Fig. 1 for the C–H stretch vibration of 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ dissolved in CD_3COCD_3 ($\nu_{\text{max}} = 2987 \text{ cm}^{-1}$). (a) 2991 cm^{-1} , (b) 2976 cm^{-1} .

delay with respect to the excitation. It has been demonstrated that the vibrational energy pumped in one of the two CH_2 stretch vibrations rapidly redistributes between the two.^{3,5,6} Because this fast redistribution of vibrational energy takes place permanently, both vibrations relax with the same time constant. Therefore, the time constants determined in Ref. 6 should correspond with our time constants for the IVR process. The time constant for CH_2I_2 of $40 \pm 5 \text{ ps}$ agrees very well with our time constant of $46 \pm 3 \text{ ps}$, but the time constant for CH_2Br_2 of $7 \pm 1 \text{ ps}$ is significantly faster than our value of $23 \pm 3 \text{ ps}$.

TABLE I. Exponential relaxation time constants for the internal vibrational relaxation (IVR) process and the intermolecular energy transfer (IET) process.

Solvent process	CCl_4		CD_3COCD_3	
	IVR	IET	IVR	IET
CH_2Br_2	$23 \pm 3 \text{ ps}$	$120 \pm 5 \text{ ps}$	$10 \pm 2 \text{ ps}$	$21 \pm 3 \text{ ps}$
CH_2I_2	$46 \pm 3 \text{ ps}$	$80 \pm 5 \text{ ps}$	$12 \pm 2 \text{ ps}$	$18 \pm 2 \text{ ps}$
$\text{C}_2\text{H}_2\text{Br}_4$	$7 \pm 2 \text{ ps}$	$95 \pm 5 \text{ ps}$	$8 \pm 2 \text{ ps}$	$12 \pm 2 \text{ ps}$

TABLE II. Widths of the Gaussians describing the low-frequency side and the high-frequency side ($\Delta\nu_2$) of the absorption band of the C–H stretch vibration ($\Delta\nu_1$) and the calculated anharmonic shifts of the maximum of the absorption band after the internal vibrational relaxation process.

Solvent	CCl ₄			CD ₃ COCD ₃		
	$\Delta\nu_1$	$\Delta\nu_2$	Shift	$\Delta\nu_1$	$\Delta\nu_2$	Shift
CH ₂ Br ₂	18 cm ⁻¹	22 cm ⁻¹	11 ± 3 cm ⁻¹	20 cm ⁻¹	20 cm ⁻¹	13 ± 3 cm ⁻¹
CH ₂ I ₂	18 cm ⁻¹	24 cm ⁻¹	11 ± 3 cm ⁻¹	20 cm ⁻¹	18 cm ⁻¹	9 ± 2 cm ⁻¹
C ₂ H ₂ Br ₄	24 cm ⁻¹	50 cm ⁻¹	18 ± 3 cm ⁻¹	38 cm ⁻¹	48 cm ⁻¹	30 ± 5 cm ⁻¹

For small molecules, the rate of energy transfer is often determined by the interaction with only a few near-resonant combination tones. For these molecules the rate is both determined by the matrix elements of the anharmonic coupling and the energy gap between the excited vibration and the combination tones. It is known from literature^{5,6} that for the dihalomethanes a strong Fermi-resonance exists between the symmetric CH₂ stretch vibration (ν_1) and the overtone of the CH₂ scissor vibration (ν_2). In addition, there are probably also strong resonances for the ν_1 of CH₂Br₂ with $2\nu_3 + \nu_8 + \nu_9$,²⁴ $\nu_2 + 2\nu_7$ and $\nu_2 + 2\nu_4 + 2\nu_9$.²⁵ In our single-color pump-probe experiments we can not identify the vibrations that are excited in the IVR process. A two-color experiment in which the color of the probe can be tuned over all the vibrations within the molecule would provide more information.

For CH₂I₂ there can be Fermi resonances with combination tones that involve more vibrational quanta than the resonances in CH₂Br₂. The energies and symmetries of the molecular vibrations of CH₂Br₂ and CH₂I₂ are presented in Table III.^{26,27} The fact that the energy gap between ν_1 and $2\nu_2$ is larger in CH₂I₂ than in CH₂Br₂ and the fact that a large change in vibrational quantum number in general slows down the relaxation,²⁸ may form the main reasons for the observation that the collective IVR of the excited asymmetric CH₂ stretch vibration (ν_6) and the symmetric CH₂ stretch vibration is two times slower for CH₂I₂ dissolved in CCl₄ than for CH₂Br₂ dissolved in CCl₄.

Both IVR and IET become much faster for CH₂Br₂ and CH₂I₂ when these molecules are dissolved in the polar solvent CD₃COCD₃. A similar acceleration of the relaxation

was observed in a previous study in which the T_2 of the symmetric CH₂ stretch vibration of CH₂Br₂ was measured in different solvents.²⁹ It turned out that in nonpolar solvents the value of the T_2 could be accurately predicted with a model in which the dephasing of the molecular vibrations is described by the fluctuations of the normal mode frequencies that are induced by the binary collisions with the solvent molecules. In this model no specific interactions between solute and solvent were taken into account.³⁰ In Lewis-base solvents like acetone or pyridine, the experimental values for T_2 were much shorter than the calculated values which can be explained from the fact that there exists a strong associative interaction between the molecules. In our experiment we observe that with CD₃COCD₃ as solvent the time constants of the IVR process of CH₂Br₂ and CH₂I₂ are approximately the same. Due to the polarity of CD₃COCD₃, there is a strong dipole-dipole and dipole-induced dipole interaction between solute and solvent. We expect that this strong interaction makes it possible to transfer the excess energy of the excited vibration with respect to the coupling combination tones to the solvent. Hence the rate of IVR can be fast in a polar solvent because it is predominantly determined by the matrix elements of the anharmonic coupling and hardly by the magnitude of the energy gap between the molecular vibrations.

For 1,1,2,2-C₂H₂Br₄, the rate of IVR is approximately the same in CCl₄ as in CD₃COCD₃, whereas the IET process is much faster in CD₃COCD₃. Apparently, this molecule has so many internal degrees of freedom that the energy gaps between the excited vibration and the coupling combination tones of other vibrations are very small. Therefore,

TABLE III. Character, symmetry, and energies of the molecular vibrations of CH₂Br₂ (Ref. 26) and CH₂I₂ (Ref. 27). The characters s and a denote symmetric and asymmetric.

Vibration	Character	Symmetry	Energy	
			CH ₂ Br ₂	CH ₂ I ₂
ν_1	CH ₂ s stretch	A ₁	2982 cm ⁻¹	2992 cm ⁻¹
ν_2	CH ₂ scissor	A ₁	1382 cm ⁻¹	1350 cm ⁻¹
ν_3	CX ₂ s stretch	A ₁	588 cm ⁻¹	484 cm ⁻¹
ν_4	CX ₂ scissor	A ₁	169 cm ⁻¹	127 cm ⁻¹
ν_5	CH ₂ twist	A ₂	1095 cm ⁻¹	1031 cm ⁻¹
ν_6	CH ₂ a stretch	B ₁	3062 cm ⁻¹	3069 cm ⁻¹
ν_7	CH ₂ rock	B ₁	812 cm ⁻¹	716 cm ⁻¹
ν_8	CH ₂ wag	B ₂	1195 cm ⁻¹	1105 cm ⁻¹
ν_9	CX ₂ a stretch	B ₂	653 cm ⁻¹	570 cm ⁻¹

even the weak interactions with a nonpolar solvent are sufficient to make the energy transfer possible.

In contrast, the IET process is enormously accelerated and is also fast compared to the IET of CH_2Br_2 and CH_2I_2 dissolved in CD_3COCD_3 . This last point may be the result of the fact that the vibrational energy is distributed over a larger molecule in the case of 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ than in the case of CH_2Br_2 and CH_2I_2 , so that the energy can be transferred to a larger number of directly surrounding solvent molecules.

When we compare the results on CH_2Br_2 and CH_2I_2 dissolved in CCl_4 with previous results on CHBr_3 and CHI_3 dissolved in CCl_4 ,²⁰ we note that the IVR process is much faster in CH_2Br_2 and CH_2I_2 than in CHBr_3 (56 ps) and in CHI_3 (95 ps). This is probably caused by the fact that the energy gap between the symmetric CH_2 stretch vibration and the overtone of the CH_2 scissor vibration is much smaller in CH_2Br_2 and CH_2I_2 than the energy gap between the C-H stretch vibration and the overtone of the C-H bend vibration in CHBr_3 and CHI_3 .

With CD_3COCD_3 as solvent, the rate of IVR is faster for CHBr_3 (5 ps) than for CH_2Br_2 . We expect that for both molecules the electrostatic interactions with the CD_3COCD_3 molecules are that strong that the rate of IVR is no longer determined by energy gaps. In CH_2Br_2 the energy pumped in the asymmetric CH_2 stretch vibration is very quickly equilibrated over symmetric and the asymmetric CH_2 stretch vibration.^{3,5,6} On the basis of symmetry only the symmetric CH_2 stretch can effectively couple with the overtone of CH_2 scissor vibration. From the model presented in Refs. 21 and 22, it follows that if two vibrations have to depopulate via one effective channel, the rate of relaxation is slowed down by a factor of 2. This effect may account for the observation that the IVR of CH_2Br_2 is slower than the IVR of CHBr_3 .

The rate of IVR of CHI_3 dissolved in CD_3COCD_3 is much slower (54 ps) than for CH_2I_2 . A possible explanation is that for CHI_3 in contrast to CH_2I_2 , the rate of IVR is still strongly determined by the energy gaps between the C-H stretch and the coupling combination tones of other vibrations, in spite of the strong interaction with the CD_3COCD_3 molecules.

We explained all the differences between CCl_4 and CD_3COCD_3 as solvent from their difference in polarity, because the polarity is very important for the amount of interaction between solute and solvent molecules. It should be noted, however, that CCl_4 and CD_3COCD_3 are different in many other aspects (size, vibrational frequencies, density of states). Therefore, future experiments with other solvents and solvent parameters may provide additional information on the influence of the solvent molecules on the rate of vibrational energy transfer.

CONCLUSIONS

We investigated the vibrational dynamics of small organic molecules in solution with ultrafast infrared saturation spectroscopy.

After excitation of the asymmetric CH_2 stretch vibration in CH_2Br_2 and CH_2I_2 and the C-H stretch vibration in

1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$, we observe that the molecules relax via two consecutive relaxation processes. In a first relaxation process a significant amount of the energy is transferred to other vibrations in the molecule that are anharmonically coupled with the excited vibration. This leads to a shift of the absorption band of the excited vibration to lower frequencies. In a second relaxation process, the energy is equilibrated over all degrees of freedom which implies that a large part of the energy is transferred to the solvent. Due to this second process the absorption band shifts back to its original value.

For CH_2Br_2 and CH_2I_2 we observe that both relaxation processes are much faster with CD_3COCD_3 as solvent than with CCl_4 as solvent. For 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ we observe that only the second relaxation process is faster with CD_3COCD_3 as solvent than with CCl_4 as solvent.

For CH_2Br_2 and CH_2I_2 dissolved in CCl_4 the energy differences between the asymmetric CH_2 stretch vibration and the coupling combination tones of other vibrations play an important role for the rate of intramolecular energy transfer, because in only very few interactions with the solvent the excess energy can be transferred to the solvent and the energy transfer becomes possible. For 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ the energy differences are very small because the molecule possesses many internal degrees of freedom so that even very weak interactions with the solvent are sufficient to make intramolecular energy transfer possible.

With CD_3COCD_3 as solvent the interactions of CH_2Br_2 , CH_2I_2 , and 1,1,2,2- $\text{C}_2\text{H}_2\text{Br}_4$ with the solvent molecules are very strong. In this case the rate of intramolecular vibrational relaxation no longer depends on the energy differences between the excited vibration and the coupling combination tones so that this rate is only determined by the matrix elements of the anharmonic coupling and the number of interacting levels.

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