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\textsubscript{2} stretch vibration of dibromomethane and diiodomethane and the C–H stretch vibration of 1,1,2,2-tetramethoxyethane. 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.\textsuperscript{1,2} 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,\textsuperscript{21,22} thus making the energy transfer possible.

In this paper we study the vibrational dynamics of the small organic molecules dibromomethane (CH\textsubscript{2}Br\textsubscript{2}), diiodomethane (CH\textsubscript{2}I\textsubscript{2}), and 1,1,2,2-tetramethoxyethane (CH\textsubscript{3}H\textsubscript{2}Br\textsubscript{4}) in a polar (CD\textsubscript{3}COCD\textsubscript{3}) and a nonpolar (CCl\textsubscript{4}) solvent.

By comparing the results on CH\textsubscript{2}Br\textsubscript{2} and CH\textsubscript{2}I\textsubscript{2}, with those on 1,1,2,2-C\textsubscript{6}H\textsubscript{4}Br\textsubscript{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\textsubscript{4} and CD\textsubscript{3}COCD\textsubscript{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.\textsuperscript{4}

The infrared pulses that we use in our experiment are generated via parametric generation and amplification in LiNbO\textsubscript{3} crystals.\textsuperscript{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\textsuperscript{-1}. The pulse duration of these pulses is approximately 20 ps and a pulse at 3000 cm\textsuperscript{-1} has a typical energy of 200 \textmu J. The bandwidth of the pulses at this wave number is approximately 15 cm\textsuperscript{-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\textsubscript{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\textsubscript{2} lens with a focal length of 5 cm, together with the strong part (pump) that was transmitted by the thin CaF\textsubscript{2} plate. Each experimental point is an average over hundreds of laser shots.

The experiments are performed with solutions of 0.1 M CH\textsubscript{2}Br\textsubscript{2} and CH\textsubscript{2}I\textsubscript{2} and 0.05 M 1,1,2,2-C\textsubscript{6}H\textsubscript{4}Br\textsubscript{4} in CCl\textsubscript{4} and CD\textsubscript{3}COCD\textsubscript{3}. We measured infrared 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\textsubscript{2} stretch vibration of CH\textsubscript{2}Br\textsubscript{2} and CH\textsubscript{2}I\textsubscript{2} and the C–H stretch vibration of 1,1,2,2-C\textsubscript{6}H\textsubscript{4}Br\textsubscript{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. 1. Relative transmission ($\ln \left( \frac{T}{T_0} \right)$) 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$_2$Br$_2$ dissolved in CCl$_4$, ($\nu_{\text{asy}} = 3062$ 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$_2$I$_2$ dissolved in CCl$_4$, ($\nu_{\text{asy}} = 3065$ 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 100–200 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$_2$Br$_2$ and CH$_2$I$_2$ and the energy of the C–H stretch vibration of 1,1,2,2-

C$_2$H$_3$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$_3$, and CHI$_3$.

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$_2$Br$_2$ and CH$_2$I$_2$ and the C–H stretch vibration of 1,1,2,2-

We conclude that...
with CCl₄ as solvent the transmission of the probe returns to its initial value for large delays. With CD₂COCD₃ 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 ± 5 K. This implies that a large part of the energy transferred to the solvent. Therefore, we 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.

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 IET 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. 3. As Fig. 1 for the C-H stretch vibration of 1,1,2,2-C₂H₂Br₄ dissolved in CCl₄ \( (ν_{max} = 2993 \text{ cm}^{-1}) \). (a) 2998 cm⁻¹, (b) 2983 cm⁻¹.

FIG. 4. As Fig. 1 for the asymmetric CH₂ stretch vibration of CH₂Br₂ dissolved in CD₂COCD₃ \( (ν_{max} = 3077 \text{ cm}^{-1}) \). (a) 3079 cm⁻¹, (b) 3053 cm⁻¹.

FIG. 5. As Fig. 1 for the symmetric CH₂ stretch vibration of CH₂Br₂ dissolved in CD₂COCD₃ \( (ν_{max} = 2953 \text{ cm}^{-1}) \). (a) 2956 cm⁻¹, (b) 2942 cm⁻¹.

FIG. 6. As Fig. 1 for the symmetric CH₂ stretch vibration of CH₂Br₂ dissolved in CD₂COCD₃ \( (ν_{max} = 2953 \text{ cm}^{-1}) \). (a) 2956 cm⁻¹, (b) 2942 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$_2$Br$_2$ and CH$_3$I$_2$ dissolved in CCl$_4$, 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 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. 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$_3$I$_2$ of 40 ± 5 ps agrees very well with our time constant of 46 ± 3 ps, but the time constant for CH$_2$Br$_2$ of 7 ± 1 ps is significantly faster than our value of 23 ± 3 ps.

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CH$_2$Br$_2$</th>
<th>CH$_3$I$_2$</th>
<th>C$_2$H$_2$Br$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>23 ± 3 ps</td>
<td>40 ± 5 ps</td>
<td>7 ± 2 ps</td>
</tr>
<tr>
<td>CD$_3$COCD$_3$</td>
<td>10 ± 2 ps</td>
<td>12 ± 2 ps</td>
<td>8 ± 2 ps</td>
</tr>
<tr>
<td>IVR</td>
<td>21 ± 3 ps</td>
<td>18 ± 2 ps</td>
<td>12 ± 2 ps</td>
</tr>
<tr>
<td>IET</td>
<td>120 ± 5 ps</td>
<td>80 ± 5 ps</td>
<td>95 ± 5 ps</td>
</tr>
</tbody>
</table>
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 that for the dihalomethanes a strong Fermi-resonance exists between the symmetric CH$_2$ stretch vibration ($v_6$) and the overtone of the CH$_2$ scissor vibration ($v_3$). In addition, there are probably also strong resonances for the $v_1$ of CH$_2$Br$_2$ with $2v_2 + v_6$, $v_3 + 2v_6$, $v_3 + v_7$, and $v_2 + 2v_6 + 2v_7$.

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 CH$_2$I$_2$ there can be Fermi resonances with combination tones that involve more vibrational quanta than the resonances in CH$_2$Br$_2$. The energies and symmetries of the molecular vibrations of CH$_2$Br$_2$ and CH$_2$I$_2$ are presented in Table III. They are larger in CH$_2$I$_2$ than in CH$_2$Br$_2$ and the fact that a large change in vibrational quantum number in general slows down the relaxation. The size of the energy gap between the excited vibration and 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-C$_2$H$_5$Br$_4$, the rate of IVR is approximately the same in CCl$_4$ as in CD$_3$COCD$_3$, whereas the IET process is much faster in CD$_3$COCD$_3$. Apparently, this molecule has so many internal degrees of freedom that the energy gaps between the excited vibrations and the coupling combination tones of other vibrations are very small. Therefore, the rate of IVR is much faster 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.

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl$_4$</th>
<th>Shift</th>
<th>CD$_3$COCD$_3$</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Br$_2$</td>
<td>18 cm$^{-1}$</td>
<td>27 cm$^{-1}$</td>
<td>11 cm$^{-1}$</td>
<td>20 cm$^{-1}$</td>
</tr>
<tr>
<td>CH$_2$I$_2$</td>
<td>18 cm$^{-1}$</td>
<td>24 cm$^{-1}$</td>
<td>11 cm$^{-1}$</td>
<td>13 cm$^{-1}$</td>
</tr>
<tr>
<td>C$_2$H$_5$Br$_4$</td>
<td>24 cm$^{-1}$</td>
<td>50 cm$^{-1}$</td>
<td>18 cm$^{-1}$</td>
<td>48 cm$^{-1}$</td>
</tr>
</tbody>
</table>

TABLE III. Character, symmetry, and energies of the molecular vibrations of CH$_2$Br$_2$ (Ref. 26) and CH$_2$I$_2$ (Ref. 27). The characters s and a denote symmetric and asymmetric.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Character</th>
<th>Symmetry</th>
<th>CH$_2$Br$_2$</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>CH$_2$ s stretch</td>
<td>$A_1$</td>
<td>2982 cm$^{-1}$</td>
<td>2992 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_2$</td>
<td>CH$_2$ scissor</td>
<td>$A_1$</td>
<td>1382 cm$^{-1}$</td>
<td>1350 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>CH$_2$ twist</td>
<td>$A_1$</td>
<td>1095 cm$^{-1}$</td>
<td>1031 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_4$</td>
<td>CH$_2$ a stretch</td>
<td>$B_1$</td>
<td>3062 cm$^{-1}$</td>
<td>3069 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_5$</td>
<td>CH$_2$ rock</td>
<td>$B_1$</td>
<td>812 cm$^{-1}$</td>
<td>716 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_6$</td>
<td>CH$_2$ wag</td>
<td>$B_1$</td>
<td>1195 cm$^{-1}$</td>
<td>1105 cm$^{-1}$</td>
</tr>
<tr>
<td>$v_7$</td>
<td>CH$_2$ a stretch</td>
<td>$B_1$</td>
<td>653 cm$^{-1}$</td>
<td>570 cm$^{-1}$</td>
</tr>
</tbody>
</table>
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 CH₂Br₂ and CH₃I dissolved in CD₃COCD₃. 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-C₂H₂Br₄ than in the case of CH₂Br₂ and CH₃I, so that the energy can be transferred to a larger number of directly surrounding solvent molecules.

When we compare the results on CH₂Br₂ and CH₃I dissolved in CCl₄ with previous results on CHBr₃ and CH₃I dissolved in CCl₄, we note that the IVR process is much faster in CH₂Br₂ and CH₃I than in CHBr₃ (56 ps) and in CHI (95 ps). This is probably caused by the fact that the energy gap between the symmetric CH₂ stretch vibration and the overtone of the CH₂ scissor vibration is much smaller in CH₂Br₂ and CH₃I than the energy gap between the C–H stretch vibration and the overtone of the C–H bend vibration in CHBr₃ and CHI.

With CD₃COCD₃ as solvent, the rate of IVR is faster for CHBr₃ (5 ps) than for CH₂Br₂. We expect that for both molecules the electrostatic interactions with the CD₃COCD₃ molecules are strong enough to make the rate of IVR no longer determined by energy gaps. In CH₂Br₂, the energy pumped in the asymmetric CH₂ stretch vibration is very quickly equilibrated over symmetric and the asymmetric CH₂ stretch vibration. On the basis of symmetry only the symmetric CH₂ stretch can effectively couple with the overtone of CH₂ 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 CH₂Br₂ is much slower than the IVR of CHBr₃.

The rate of IVR of CHI dissolved in CD₃COCD₃ is much slower (54 ps) than for CH₂Br₂. A possible explanation is that for CHI in contrast to CH₂Br₂, 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 CD₃COCD₃ molecules.

We explained all the differences between CCl₄ and CD₃COCD₃ 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 CCl₄ and CD₃COCD₃ 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 CH₂ stretch vibration in CH₂Br₂ and CH₂I₂ and the C–H stretch vibration in 1,1,2,2-C₂H₂Br₄, 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 CH₂Br₂ and CH₃I, we observe that both relaxation processes are much faster with CD₃COCD₃ as solvent than with CCl₄ as solvent. For 1,1,2,2-C₂H₂Br₄ we observe that only the second relaxation process is faster with CD₃COCD₃ as solvent than with CCl₄ as solvent.

For CH₂Br₂ and CH₃I dissolved in CCl₄ the energy differences between the asymmetric CH₂ stretch vibration and the coupling combination tones of other vibrations play an important role for the rate of intramolecular energy transfer, because in 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-C₂H₂Br₄ 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 CD₃COCD₃ as solvent the interactions of CH₂Br₂, CH₂I₂, and 1,1,2,2-C₂H₂Br₄ 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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