Ultrafast infrared saturation spectroscopy of chloroform, bromoform, and iodoform

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In this paper we present a study of the vibrational energy relaxation processes of chloroform, bromoform, and iodoform in solution after excitation of the C-H stretch vibration. The relaxation is studied with ultrafast infrared saturation spectroscopy using intense infrared pulses with a pulse duration of 19 ps. The experiments were performed in a polar and a nonpolar solvent in order to study the effects of the polarity of the solvent on the relaxation processes. We observe that in both types of solvent the relaxation takes place via two consecutive relaxation processes and that the relaxation leads to ultrafast changes of the absorption band of the C–H stretch vibrations. We discuss the differences in the time constants of the relaxation processes of the halofoms in terms of the energy differences between the vibrational levels and the interactions with the solvent.

I. INTRODUCTION

During the last decades many time-resolved studies on the vibrational dynamics of small molecules in the electronic ground state have been performed with a variety of techniques. These studies are mostly concerned with the processes of relaxation after excitation of one of the molecular vibrations. In time-resolved studies, the decay of the excitation is studied by probing the system as a function of the delay with respect to the excitation. The molecular vibration can efficiently be excited in a one-photon process, if the dipole moment of the molecule changes as a result of the vibrational motion. This type of excitation requires, in general, an infrared light source. It is possible to use visible light sources if the vibration is excited with nonlinear optical techniques like stimulated Raman scattering. In this technique the frequency difference of two coherent light beams corresponds with the energy difference between the ground state and the excited state of the molecular vibration.

Provided that the vibration is coherently excited, it is possible to study the decay of the coherence of the excitation. This decay is the result of both the dephasing of the excited oscillators and the energy relaxation of the excited state of the molecules. The time constant of the decay of the coherence can be determined by probing the excitation with techniques like stimulated Raman scattering and coherent anti-Stokes Raman scattering or by measuring the free-induction decay of the exciting pulses. The disadvantage of these techniques is that no distinction can be made between relaxation due to dephasing and relaxation due to energy relaxation.

The time constant of the energy relaxation of the molecules can be measured with probing techniques that are not sensitive for the relative phases of the excited oscillators but are only sensitive for the amount of population of the excited state. These techniques can also be applied if the vibration is excited incoherently. Among these techniques are spontaneous anti-Stokes Raman scattering, infrared saturation spectroscopy, and double-resonance spectroscopy.

In the past, the energy relaxation of many molecular vibrations like C=O, C–H, O–H stretch vibrations have been studied with spontaneous anti-Stokes Raman scattering and infrared saturation spectroscopy. In all these studies the time constant of the relaxation was determined, but in only a few of these studies information on the channels of relaxation could be obtained. More recently, double-resonance spectroscopy has been developed and this technique turned out to be very useful in obtaining information on the relaxation channels of excited molecular vibrations.

In this paper we study in detail with infrared saturation spectroscopy the relaxation channels of chloroform (CHCl₃), bromoform (CHBr₃), and iodoform (CHI₃) after excitation of the C–H stretch vibration. These halofoms are very suitable systems to study vibrational energy-transfer processes because they possess a relatively small number of molecular vibrations (compared to other organic molecules) and the strong anharmonic coupling of these vibrations.

In two previous studies, it was deduced with double-resonance spectroscopy that the first excited state of the C–H stretch vibration of CHBr₃ dissolved in CCl₄ relaxes via two consecutive relaxation processes. In a first process a large part of the vibrational energy is transferred to other vibrations within the molecule. In a second process, the energy of the other molecular vibrations is mainly transferred to the solvent.

In this paper we present experimental results on the same system from which we can deduce the time constants of both relaxation processes. We compare these results with those obtained with double-resonance infrared spectroscopy.

In addition, we study the energy-transfer processes of CHCl₃ and CHI₃ dissolved in CCl₄ and we compare these with CHBr₃. We discuss the effect of the energy differences between the C–H stretch vibration and the other vibrations in the molecule on the first relaxation process.
Finally, the haloforms are dissolved in deuterated acetonitrile ($CD_3CN$) so that the influence of the polarity of the solvent on the energy-transfer processes can be studied. We observe that in $CD_3CN$ the energy transfer leads to an ultrafast change in the interaction between the haloform molecule and the surrounding solvent molecules.

II. EXPERIMENT

A. Infrared saturation spectroscopy

Infrared saturation spectroscopy is based on the excitation of a significant fraction of the molecules with an intense infrared pulse. This results in a transient bleaching of the sample. This bleaching can be probed by measuring the transmission of a weak second pulse of the same frequency. If this probe pulse is so weak that it does not significantly change the populations, its transmission can be described by the law of Lambert-Beer:

$$T(\tau) = T_{\text{ref}} e^{-\alpha c(\tau)l},$$

with $\tau$ the delay between pump and probe, $T(\tau)$ the transmitted energy of the probe, $T_{\text{ref}}$ the input of the probe, $\alpha$ the molecular absorption coefficient, $c(\tau)$ the concentration of molecules that can absorb the light of the probe, and $l$ the length of the sample.

For $c(\tau)$ we can use the following expression:

$$c(\tau) = c_0 (1 - 2fp(\tau)),$$

with $c_0$ the concentration of molecules that are available for absorption before the pump enters the sample, $f$ the fraction of molecules that is excited by the pump, and $p(\tau)$ the function that describes the relaxation of the excited molecules as a function of the delay between pump and probe. When we substitute Eq. (2) into Eq. (1) we obtain the following expression:

$$\ln \left[ \frac{T(\tau)}{T_{\text{ref}}} \right] + \alpha c_0 l = \ln \left[ \frac{T(\tau)}{T_{\text{ref}}} \right] - \ln \left( \frac{T_0}{T_{\text{ref}}} \right) 2 \alpha c_0 f p(\tau).$$

If the studied vibration can be described as an exponentially relaxing two-level system, the function $p(\tau)$ is equal to $e^{-\tau/T_1}$, with $T_1$ the population relaxation time constant, for delays that are much larger than the pulse duration. The relaxation of the initially excited vibration can also lead to the excitation of other vibrations in the molecule. This excitation may induce a change of the transition frequency of the first vibration, if the vibrations are anharmonically coupled. In case the transition frequency is shifted, the absorption coefficient for the probe pulse changes, and the transmission of the probe pulse will not return to its original value after population relaxation of the initially excited vibration. This transient change of the absorption coefficient makes it possible to determine both the time constant of the relaxation of the initially excited vibration and the time constants of subsequent relaxation channels.

B. Generation of tunable infrared pulses

The infrared pulses are generated by means of parametric generation and amplification in LiNbO$_3$ crystals. In these processes a very intense pulse at frequency $\omega_1$ (pump) is converted into two other light pulses at $\omega_1$ (signal) and $\omega_2$ (idler) under the condition $\omega_3 = \omega_1 + \omega_2$. By convention, the frequency of the signal is always equal to or higher than that of the idler. The experimental set-up is depicted schematically in Fig. 1. The pump laser for the parametric generation and amplification processes is provided by a mode-locked Nd:YAG (where YAG denotes yttrium aluminium garnet) laser. This laser produces pulses with a pulse duration of 35 ps and an energy of approximately 35 mJ at a wavelength of 1064 nm. The repetition rate of the system is 10 Hz. The pulses are split in three. The first pulse with an energy of 6 mJ pumps a single-pass parametric generator consisting of a 5 cm LiNbO$_3$ crystal with its optical axis cut at 47.1$^\circ$. After this crystal, the pump pulse and the generated idler are blocked. The signal pulse is amplified in a 2 cm
LiNbO₃ crystal with a new synchronized pump pulse with an energy of 9 mJ. After this second crystal, the pump pulse and the generated idler are blocked again. It is more profitable to amplify the signal rather than the idler because the optical components that block and reflect the Nd:YAG pulse strongly absorb the idler.

Finally, the signal pulse is amplified in a third 3 cm LiNbO₃ crystal with the third pump pulse with an energy of 8 mJ. After this last crystal, only the pump pulse is blocked. The signal is used to analyze the generated frequencies of signal and idler. In order to do this, the second harmonic of the signal is generated in a BBO crystal cut at 22.8°. The frequency of this second harmonic is analyzed by a spectrograph in combination with an optical multichannel analyzer. The idler is used for the experiment.

With this setup intense infrared pulses can be generated in the frequency range of 2200–7200 cm⁻¹. The generated pulses have a pulse duration of approximately 19 ps. An idler pulse at 3000 cm⁻¹ has a typical energy of 200 µJ. The bandwidth of the pulses generated at this frequency is approximately 15 cm⁻¹, which implies that the pulses are not bandwidth limited.

C. Pump–probe setup

In Fig. 2 the experimental setup for performing pump–probe experiments is schematically depicted. The idler pulse is split into two pulses by a thin CaF₂ plate (0.5 mm) which has a reflectance of 1% and a transmittance of 99%. The reflected pulse (probe) is sent into a variable delay. This consists of a cold-coated open retroreflector on a translation stage. By moving the retroreflector 1 mm back, the probe is delayed 6.67 ps. After the variable delay, 1% of the probe pulse is reflected by a second CaF₂ plate on a roughened aluminum plate which reflects this beam diffusely. The diffused light is detected by a PbSe photoconductive cell (detector 2). The beam is diffused, because the beam has spatial features that fluctuate from shot to shot. If the beam would be detected directly, these spatial features would cause extra fluctuations because the detectors have a limited sensitive area. Before the PbSe cell a germanium long-wave pass filter is placed that only transmits the idler. The signal of this detector is used as a reference of the intensity that enters the sample. The probe is focused into the sample by a CaF₂ lens with a focal length of 5 cm together with the strong pump pulse that is transmitted by the first CaF₂ plate. The sample cell has a length of 1 mm. After the sample, the beams are made parallel again with a second 5 cm CaF₂ lens. The intensity of the transmitted probe is detected by detector 1 in the same way as the reference.

The whole experiment is computer controlled. A typical experiment consists of 20 scans of the variable delay over 50 or 100 mm. Each scan consists typically of 51 points of delay. The position of the delay is accurately determined (within 1 µm) with a magnetic ruler. At each point of delay the transmission of the probe and the reference signal of 20 laser shots are stored.

D. Sample preparation

The experiments are performed with dilute solutions of the haloforms in CCl₄ and CD₄COCD₃. We use CD₂COCD₃ for the polar solvent instead of CH₃COCH₃ because the C–H vibrations of CH₃COCH₃ absorb at approximately the same wavelength as the C–H stretch of CH₂Cl₂, CHBr₂, and CHI₃. We use 0.1 mol/l solutions of CHCl₃ and CHBr₃ in CCl₄.

CHI₃ is a solid at room temperature and is hardly soluble in CCl₄. We also note that upon solving CHI₃ in CCl₄ the solution obtains a red color which indicates that CHI₃ reacts with CCl₄ and forms ICl. However, after a few
minutes we noticed that this reaction reaches an equilibrium and the concentration CHI remains stable. Only a small amount of ICl and other products is formed so that these products do not disturb the experiment. Although the concentration of CHI is very low (below 0.01 mol/l), so that only a small fraction of the pulses is absorbed, the transmission changes are still large enough to perform the experiment. This is mainly due to the high molecular absorption coefficient and the large relaxation time constants of CHI dissolved in CCl4.

The haloforms can all be solved well in CD2COCD3. We use 0.1 mol/l solutions of CHCl3 and CHBr3 and a 0.05 mol/l solution of CHI3. We measure ir spectra of all samples using a double-beam Perkin-Elmer 881 spectrometer with a resolution of 1.2 cm⁻¹ in order to check the optical density and to determine the maximum and the width of the absorption band of the C–H stretch vibration.

III. RESULTS AND DISCUSSION

A. Vibrational dynamics of the haloforms of CCl4

In our experiment we tune the central frequency of the laser pulses through the absorption band of the C–H stretch vibration. For each frequency we measure the relative transmission of the probe pulse as a function of the delay between pump and probe. In Figs. 3, 4, and 5 typical results are presented for CHCl3, CHBr3, and CHI3 dissolved in CCl4. We observe that when the probe overlaps in time with the pump, the transmission of the probe increases because of the bleaching of the sample due to the pump. For larger delay times the transmission decreases due to the relaxation.

In Figs. 3(b), 4(b), and 5(b) the central frequency of the pulses is lower than the maximum of the absorption band. We observe for CHCl3 [Fig. 3(b)] and CHBr3 [Fig. 4(b)] that the transmission decreases to a value lower than the one before excitation by the pump. For CHI3 [Fig. 5(b)], we do not observe such an overshoot, but we do observe a steepening of the transmission decrease compared to the case in which the central frequency of the laser pulse was higher than the maximum of the absorption band [Fig. 5(a)]. The overshoot and the steepening of the decrease in transmission indicate that the transition frequency shifts to a lower value and better into resonance with the spectrum of the probe. Such a shift is very likely due to the excitation of other vibrational modes within the molecules that are anharmonically coupled to the C–H stretch vibration. For larger delay times the transmission rises again to its initial value, which indicates that these other vibrations lose their energy. We deduce from these results that for all three haloforms the relaxation takes place via two consecutive relaxation processes. In the first process, a significant amount of the vibrational energy is transferred from the C–H stretch vibration to other modes in the molecule that couple with the C–H stretch vibration. In the second process, these other vibrations transfer the energy to the solvent molecules or to lower-lying vibrations within the molecule that do not influence the C–H stretch vibration. The results with CD2COCD3 as solvent, presented in the following subsection, indicate that in this second process the energy is equilibrated over all degrees of freedom, which implies that a large part of the energy is transferred to the solvent. Although the two relaxation processes are not purely intramolecular and intermolecular, respectively, we will refer to these processes in the following as internal vibrational relaxation (IVR) and intermolecular energy transfer (IET). If the central frequency of the laser pulses is as high as or higher than the maximum of the absorption band [Figs. 3(a), 4(a) and 5(a)], the transition shifts out of the bandwidth of the laser pulse after the IVR process. The result is that the transmission remains increased as long as the molecules have not relaxed via the IET process.

The IET process results in a rise of the local temperature. This rise in temperature may, in principle, lead to a change of the absorption coefficient and thus to an increased or decreased transmission level for large delay times. We observe that in all cases the transmission of the probe returns to its initial value. This is in good agreement with the fact that the absorption band of the haloforms...
dissolved in CCl₄ hardly changes if the temperature is increased. In contrast, in Ref. 32 an increased transmission level for long delay times for CHBr₃ dissolved in CCl₄ was observed. In that experiment a very high concentration of CHBr₃ in CCl₄ was used (3.7 mol/l). This high concentration can lead to a change of the absorption band due to the mutual interaction of the dipoles of the CHBr₃ molecules. This mutual interaction may very well be temperature dependent. In addition, the higher concentration of CHBr₃ also leads to a larger rise of the temperature.

The time constants of the relaxation processes can be deduced by comparing the experimental results with numerical calculations. We calculate the absorption of pump and probe in the sample using a simple four-level system (Fig. 6). 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 two relaxation processes. In this model all the other vibrations that are excited in the IVR process are combined into one level. This implies that we assume in the calculation that the combined excitation of all these vibrations can be described as a change of the absorption coefficient and that this change relaxes via a single exponential. In reality it can be expected that each of the vibrations induces a change of the absorption coefficient and that the overall change that is measured in the experiment relaxes via a sum of exponentials.

In all figures the calculated results represented by the solid curves are in good agreement with the experimental results. The time constants of the relaxation are presented in Table I. In two previous studies on CHCl₃, a time constant of the relaxation of the C-H vibration was measured with spontaneous anti-Stokes Raman scattering. These reported time constants, 2.5 ±0.5 ps¹⁸ and 1.6 ps,¹⁹ are both
much smaller than our value of 30±2 ps for the IVR process. In these studies no experimental information was obtained on the relaxation channels. For CHBr₃, the time constants of the two relaxation processes were measured previously with spontaneous anti-Stokes Raman scattering and double-resonance spectroscopy. These time constants, 40±5, 23 45±7, 19 and 40±5 ps for the IVR process and 190±40 ps for the IET process, are somewhat shorter than our time constants of 56±2 ps and 260±10 ps. This may be caused by the fact that in all these experiments the concentration CHBr₃ was higher than in our experiment, leading to a stronger mutual interaction of the dipoles of the CHBr₃ molecules. We will show in the following subsection that a strong intermolecular interaction can significantly shorten the relaxation times.

The magnitude of the shift of the transition frequency after the IVR process can be determined from the absorption coefficients that are used in the numerical simulations. The absorption coefficient is a function of the shape of the absorption band, the spectral shape of the laser pulses, and the detuning of the central frequency of the laser pulses with respect to the maximum of the absorption band. Because the absorption band is asymmetric, we model it with two half-Gaussians with different widths. We use the following equation for the absorption coefficient:

$$\beta = C \left( \frac{\Delta v_1}{C} \exp \left[ -4 \ln 2 (\frac{v}{\Delta v_1})^2 \right] - \delta \right) \exp \left[ -4 \ln 2 (\frac{v}{\Delta v_2})^2 \right]$$

$$\times \exp \left[ -4 \ln 2 (\frac{v - \delta}{\Delta v_2})^2 \right],$$

(4)

with $\beta$ proportional to the absolute absorption coefficient $\alpha$, $C$ proportional to the transition dipole moment, $\Delta v_1$ the width at half maximum of the Gaussian describing the low-frequency side of the absorption band, $\Delta v_2$ the width of the Gaussian describing the high-frequency side, $\Delta v_1$ the width of the Gaussian describing the spectrum of the pulses, and $\delta$ the detuning. The values of $\Delta v_1$ and $\Delta v_2$ are determined from absorption spectra.

With the initial values of $\beta$ and $\delta$ the value of $C$ can be determined. If we assume that $C$ does not change after the absorption band has shifted due to the IVR process, the value of $\beta$ after the shift can be used to determine the new value of $\delta$. This new $\delta$ minus the initial one gives the shift of the absorption band. This shift should be independent of the central frequency of the laser pulses. The calculated shifts and the widths $\Delta v_1$ and $\Delta v_2$ are presented in Table II.

The shift of the transition frequency of CHBr₃ agrees very well with the shift reported in Refs. 29 and 32. The shift of CHCl₃ is larger than that of CHBr₃ and leads to a larger dip in the transmission of the probe, if we choose the frequency of the laser pulses below the maximum of the absorption band. Although the shift of CHI₃ is somewhat larger than the shift of CHBr₃, we do not observe a dip in the transmission of the probe. This can be explained from the fact that the magnitude of the dip is also determined by the ratio of the relaxation time constants of the IVR process and the IET process and the initial detuning of the laser pulse. If this ratio is small (fast IVR, slow IET) the dip will be large. In CHI₃ this ratio is comparatively large and the detuning of the pulses in Fig. 5(b) is rather small. The experiment cannot be performed with a larger detuning because the relative changes in the transmission of the probe are small due to the fact that the concentration CHI₃ that can be solved in CCl₄ is very low.

The rate of IVR is determined by the anharmonic coupling between the excited C–H stretch vibrations and the near-resonant combination tones of other vibrations. In a liquid this rate is significantly accelerated by the intermolecular interactions because these interactions couple with the vibrational modes so that it becomes possible to transfer the excess energy of the C–H vibration with respect to the combination tones into rotational or translational energy. 26 This implies that already in the first process part of the energy of the C–H stretch vibration is transferred to the solvent. These interactions can be viewed as fluctuations of the vibrational energy levels and make that the levels obtain equal energies so that energy transfer becomes possible.

We observed that the IVR process becomes slower going from CHCl₃ to CHBr₃ to CHI₃. This can be due to two effects that result from the fact that the energy differences

<table>
<thead>
<tr>
<th>TABLE I. Exponential relaxation time constants for the internal vibrational relaxation (IVR) process and the intermolecular energy transfer (IET) process.</th>
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<tbody>
<tr>
<td>Solvent process</td>
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<tr>
<td>-----------------</td>
</tr>
<tr>
<td>CHCl₃</td>
</tr>
<tr>
<td>CHBr₃</td>
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<tr>
<td>CHI₃</td>
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</tbody>
</table>

<p>| TABLE II. Widths of the Gaussians describing the low-frequency side ($\Delta v_1$) and the high-frequency side ($\Delta v_2$) of the absorption band of the C–H stretch vibration and the calculated anharmonic shifts of the maximum of the absorption band after the interna vibrational relaxation process. |
|-----------------|------|------|------|------|------|------|------|------|</p>
<table>
<thead>
<tr>
<th>Solvent process</th>
<th>CHCl₃</th>
<th>CHBr₃</th>
<th>CHI₃</th>
<th>CCl₄</th>
<th>CD₃COCD₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta v_1$</td>
<td>14</td>
<td>12</td>
<td>20</td>
<td>16</td>
<td>36</td>
</tr>
<tr>
<td>$\Delta v_2$</td>
<td>20</td>
<td>16</td>
<td>11±3</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>Shift ($\text{cm}^{-1}$)</td>
<td>17±3</td>
<td>10±2</td>
<td>8±2</td>
<td>5±2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>36</td>
<td>10±2</td>
<td>28</td>
<td></td>
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</tbody>
</table>
TABLE III. Character, symmetry and energies required to excite the first excited state of the molecular vibrations of CHCl₃, CHBr₃, and CHI₃. The characters s and d denote symmetric and degenerate.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Character</th>
<th>Symmetry</th>
<th>CHCl₃ (cm⁻¹)</th>
<th>CHBr₃ (cm⁻¹)</th>
<th>CHI₃ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁</td>
<td>C-H s stretch</td>
<td>A₁</td>
<td>3021</td>
<td>3032</td>
<td>3013</td>
</tr>
<tr>
<td>ν₂</td>
<td>CX₃ s stretch</td>
<td>A₁</td>
<td>680</td>
<td>541</td>
<td>425</td>
</tr>
<tr>
<td>ν₃</td>
<td>CX₃ s deform</td>
<td>A₁</td>
<td>363</td>
<td>222</td>
<td>154</td>
</tr>
<tr>
<td>ν₄</td>
<td>C-H d bend</td>
<td>E</td>
<td>1220</td>
<td>1149</td>
<td>1068</td>
</tr>
<tr>
<td>ν₅</td>
<td>CX₃ d stretch</td>
<td>E</td>
<td>774</td>
<td>669</td>
<td>578</td>
</tr>
<tr>
<td>ν₆</td>
<td>CX₃ d deform</td>
<td>E</td>
<td>261</td>
<td>155</td>
<td>110</td>
</tr>
</tbody>
</table>

between the C-H stretch vibration and the other vibrations in the molecule increase going from CHCl₃ to CHBr₃ to CHI₃. In the first place, an increase of these differences requires a larger change in vibrational quantum numbers when the energy is transferred from the C-H stretch vibration to the other vibrations in the molecule, which leads to a decrease of the matrix elements of the anharmonic coupling. In the second place, the amount of fluctuations during which energy transfer becomes possible depends on the difference in energy between the vibrational levels and becomes smaller with increasing energy difference.

The character and energies of the molecular vibrations in the haloforms are presented in Table III. It is not possible from our experimental results to determine which vibrations are excited after the IVR process. It is known that molecular vibrations with the same symmetry show the largest anharmonic coupling. Theoretical studies show that there is a strong Fermi resonance between the C-H stretch vibration and the first overtone of the C-H bend vibration (ν₄). In Ref. 32 comparison of the relaxation time constant of the IET process of CHBr₃ with ultrasonic dispersion measurements suggested that the symmetric CBr₃ stretch vibration (ν₂) is excited after the IVR process. Therefore, it seems probable that a large part of the vibrational energy of the C-H stretch vibration is transferred to the first overtone of the C-H bend vibration (ν₄) combinations of ν₂ and the symmetric CX₃ deforming vibration ν₃.

The observed shift of the absorption band and the time constant of the IET process are weighted averages over all the molecular vibrations that are excited in the IVR process. If a vibration relaxes very fast, its influence on the transmission of the probe will be small because it can only influence this transmission during a very short period of time. The contribution of such a vibration to the observed shift of the absorption band will be strongly smeared out in time because molecules in the sample are continuously excited during the time that the pump pulse is present. In addition, the IVR is not an instantaneous process. Therefore, our results suggest that if the C-H bend vibration is excited in the IVR process, it relaxes very fast because it is known that, in principle, the excitation of the C-H bend vibration introduces much larger anharmonic shifts than the shifts we observed.

B. Vibrational dynamics of the haloforms in CD₃COCD₃

In Figs. 7, 8, and 9 typical results of the relative transmission of the probe as a function of the delay are presented for CHCl₃, CHBr₃, and CHI₃ dissolved in CD₃COCD₃. We observe again that for CHCl₃ (Fig. 7) and CHBr₃ (Fig. 8) the relative transmission of the probe strongly depends on whether the central frequency of the laser pulses is above or below the maximum of the absorption band of the C-H stretch vibration. We deduce that the relaxation again takes place via two processes. The first is dominated by internal vibrational relaxation and the second is dominated by intermolecular energy transfer.

The use of CD₃COCD₃ as a solvent leads to two important differences compared with CCl₄. In the first place, the relaxation processes take place on a much shorter time scale. In the second place, we observe that for large delay times the relative transmission of the probe remains at an increased level if the central frequency of the laser pulses is initially below the maximum of the absorption band.

Both effects are the result of the fact that the large dipole moment of the CD₃COCD₃ molecules leads to a
much stronger interaction of the haloform molecules with the solvent molecules. This stronger interaction is reflected in the larger width of the absorption band of the C–H vibration. The interaction strongly couples to the vibrational modes and induces large fluctuations of the energy levels of the molecular vibrations so that during a large amount of fluctuations the energy transfer becomes possible. We have studied the temperature dependence of the absorption band of the C–H stretch vibration in CD$_2$COCD$_3$ and noted that an increase in temperature leads to a steepening of the low-frequency side of the absorption band. The observation of an increased transmission level for large delay time in Figs. 7(b), 8(b), and 9(b) indicates that the second process leads to a rise in temperature. This implies that in the second process the energy is equilibrated over all degrees of freedom and that a large part of the energy is transferred to the solvent. The increased transmission level remains constant on a picosecond time scale because the solvent molecules have to lose their energy via diffusion which typically takes place within nanoseconds or microseconds. From the study of the temperature dependence of the absorption band it follows that the increased transmission level corresponds with an average rise of the temperature in the focus of 30 ± 5 K.

The time constants of both the internal vibrational relaxation process and the intermolecular energy transfer process can be determined by comparing the experimental results with numerical simulations on a six-level system (Fig. 10). The resulting time constants are presented in Table I. We note that it is possible to determine accurately time constants that are much smaller than the pulse duration if the two relaxation processes have an opposite effect on the transmission of the probe [Fig. 7(b) and 8(b)].
With CD$_2$COCD$_3$ as the solvent, we observe that for CHCl$_3$ and CHBr$_3$ the rate of IVR is much faster than with CCl$_4$ as solvent and that the time constants of this process are approximately the same. A possible explanation for this observation is that in CD$_2$COCD$_3$, the induced fluctuations are large compared to energy differences between the excited C-H stretch vibration and the near-resonant combination tones, so that these energy differences hardly influence the amount of fluctuations during which energy transfer becomes possible.

For CH$_3$, we observe that the relative transmission of the probe hardly depends on whether the central frequency of the laser pulses is above or below the maximum of the absorption band. It is possible that in this case the dip or steepening cannot be observed because the time constant of the IVR process is very large compared to that of the IET process. In this case the absorption band is shifted for those molecules that have relaxed via the IVR process, but these molecules relax too fast via the IET process to have a significant influence on the transmission of the probe. This makes it possible to determine the shift of the absorption band after the IVR process and the time constant of the IET process.

A possible explanation for the slow IVR is that for CH$_3$ the influence of the interaction with the CD$_2$COCD$_3$ molecules on the C-H stretch vibration will be small due to the small dipole moment of CH$_3$. This slow IVR makes it easy to saturate the excitation which agrees with the observation that the relative transmission changes of the probe can be as large as 500%.

In contrast to the IVR process, the IET process is significantly accelerated with CD$_2$COCD$_3$ as solvent. In the IET process the vibrational energy is transferred to vibrations involving iodine atoms. These iodine atoms have a large electrical polarizability so that they will have a strong dipole-induced-dipole interaction with the CD$_2$COCD$_3$ molecules. This relatively strong interaction makes it possible that these other vibrations quickly transfer their energy to the solvent.

**IV. CONCLUSIONS**

In this paper we have used ultrafast saturation spectroscopy to study the vibrational dynamics of CHCl$_3$, CHBr$_3$, and CH$_3$ after excitation of the C-H stretch vibration. We deduce from our results that both in a nonpolar (CCl$_4$) and a polar (CD$_2$COCD$_3$) solvent, the C-H stretch vibration relaxes via two consecutive relaxation processes. In a first process a large part of the energy is transferred to other vibrations with lower energies within the molecule [internal vibrational relaxation (IVR)]. In the second process a large amount of the energy is transferred from the other vibrations to the solvent molecules [intermolecular energy transfer (IET)]. After the IVR process the maximum of the absorption band of the C-H stretch vibration is shifted to a lower value.

We observe that with CCl$_4$ as a solvent, the time constants of the relaxation processes become larger when the energy differences between the C-H stretch vibrations and the other vibrations increase. With CD$_2$COCD$_3$ as a solvent, we observe for CHCl$_3$ and CHBr$_3$ that the IVR process is strongly accelerated and that the rate of IVR is approximately the same. This is probably the result of the fact that the strong dipole–dipole interaction with the solvent leads to fluctuations of the coupled levels that are large compared to the energy differences between the levels.

A probable explanation for the results on CH$_3$ dissolved in CD$_2$COCD$_3$ is that the IVR process is only slightly accelerated by the interaction with the solvent, while the IET process is strongly accelerated. This difference in acceleration can be explained from the fact that the dipole–dipole interaction of CH$_3$ with CD$_2$COCD$_3$ will be small due to the small permanent dipole moment of CH$_3$, while the dipole-induced-dipole interaction will be large due to the large electrical polarizability of the iodine atoms.

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