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Effect of intermolecular interactions on vibrational-energy transfer in the liquid phase

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We present an experimental and theoretical study of the relaxation after excitation of the C–H stretch vibration for dilute solutions of CHCl_3 , CHBr_3 , and CHI_3 dissolved in different solvents and for the pure liquids CHCl_3 and CHBr_3 . Experimentally, we study the relaxation with pump–probe experiments using picosecond infrared pulses and we found that the vibrational-energy transfer takes place via an intramolecular vibrational-relaxation process followed by an intermolecular energy transfer. Theoretically, we develop a new model for the description of intramolecular vibrational energy transfer. In this model the important effects of the *intermolecular* interactions on the rate of *intramolecular* energy transfer are described. From the comparison between experiment and theory the relevant parameters for intramolecular vibrational-energy transfer can be identified.

INTRODUCTION

Over the past decades many time-resolved studies employing ultrashort light pulses have been devoted to the study of the time scale and channels of relaxation of excess vibrational energy of small organic molecules. Many of these studies use strong picosecond ir laser pulses to excite a molecular vibration and a delayed probing process to monitor the rate of decay of the excitation.^{1–22} In several studies it was found that after excitation of a high-frequency molecular vibration, the molecule relaxes via two consecutive relaxation processes.^{7,8,14,15,17–22} In a first, *intramolecular* vibrational-relaxation (IVR) process, a large part of the energy is transferred from the excited vibration to other vibrations within the molecule. This excitation of other vibrational modes within the molecule that are anharmonically coupled with the initially excited vibration can lead to a shift of the absorption band of the vibration that was initially excited. In a second, *intermolecular* relaxation process, the energy is transferred from the excited molecule to the surrounding molecules.

The shift of the absorption band after the IVR process can be so large that the absorption band shifts completely out of the bandwidth of the ir pulse, as is observed after excitation of the symmetric CH_3 vibration of CH_3S chemisorbed to Ag (1,1,1).^{15,17} In previous infrared pump–probe experiments on dihalo and trihalomethanes (haloforms)^{19–21} it was found that the frequency shift of the absorption band leads to a transient increase or decrease of the absorption coefficient. In these studies^{19–21} it was observed that the relaxation time constants of the IVR process strongly depend on the nature of the solvent. In this paper we investigate the effect of the solvent on the vibrational relaxation in more detail and we present a new theoretical model for IVR in which the important effects of *intermolecular* interactions on *intramolecular* energy transfer are accounted for. By comparing the measured rate

constants for the IVR process with the calculated results based on this model we can identify the relevant parameters that determine the rate of IVR of small molecules in the liquid phase.

EXPERIMENT

The experiments are performed using a single-color infrared pump–probe technique.² In this technique a molecular vibration is first saturated with an intense infrared pulse (pump). Second, the transmission of a weak pulse (probe) is measured as a function of the delay with respect to the first pulse and thereby the decay of the excitation is monitored. The experimental setup is described in detail in Ref. 20. The ir pulses are generated via parametric generation and amplification in three 5 cm LiNbO_3 crystals (cut at 47.1 degrees).^{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). This setup generates pulses that are tunable from 2200 to 7200 cm^{-1} (1.4–4.5 μm) with a pulse duration of 20 ps. A pulse at 3000 cm^{-1} has a typical energy of 200 μJ . The bandwidth of the pulses at this frequency is approximately 15 cm^{-1} , which implies that the pulses are not bandwidth limited. A small part of the generated ir pulse is reflected by a beam sampler and sent into a variable delay. This part serves as the probe in the pump–probe experiment. The strong remaining part of the pulse serves as the pump. Pump and probe are focussed with a 5 cm CaF_2 lens into the same volume of a sample cell.

The experiments are performed with dilute solutions of chloroform (CHCl_3), bromoform (CHBr_3) and iodoform (CHI_3) dissolved in *d*-chloroform (CDCl_3) and *d*6-benzene (C_6D_6) using a sample length of 1 mm. We used the deuterated analogs of CHCl_3 and C_6H_6 because the C–H vibrations of these molecules absorb in the same frequency regime as the haloforms. When CHI_3 is solved in CDCl_3 , the solution obtains a red color indicating that a reaction takes place in which ICl is formed. We deduce from the

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conventional ir absorption spectrum that only a very small amount of ICI and other products is formed. These products have no measurable influence on the experiment. For the experiments on pure CHCl_3 and pure CHBr_3 we used a much shorter sample length of 0.05 mm. We measured ir absorption spectra of all samples prior to the time-resolved experiments to check the optical density and to determine the maximum and shape of the absorption band.

THEORETICAL MODEL FOR IVR

In the past several theoretical models describing vibrational relaxation in the condensed phase have been developed.^{24–29} The theory of Nitzan and Jortner²⁴ describes the relaxation of an excited vibration to several accepting modes. This theory can also be used for an intramolecular vibrational relaxation (IVR) process in which one of the accepting modes is an anharmonically coupled combination tone of intramolecular vibrations.²⁵ The energy mismatch between the excited vibration and the anharmonically coupled combination tone is transferred to accepting modes of the surroundings which can be phonons of a crystal or degrees of freedom of a liquid. Also in the models for IVR in liquids developed by Fisher *et al.*^{26,27} and Velsko and Oxtoby,^{28,29} the energy mismatch is compensated by the solvent. In these models this compensation is described classically using an independent binary collision model^{26–29} or a hydrodynamic model.²⁸

In all these previous models the anharmonic coupling should depend explicitly on the solvent coordinates to induce a change of the state and energy of the solvent in the IVR process. A serious problem in these descriptions is that the anharmonic coupling will be only weakly solvent dependent since it describes an intramolecular interaction. However, the modification of the vibrational state (by excitation or by IVR) itself can lead to a change of the interaction between molecule and liquid and thereby to a change of the solvent states. This means that the state and energy of the solvent can get modified in the IVR process, although the anharmonic coupling itself does not depend on the solvent coordinates.

We will use this latter effect to describe the solvent dependence of the IVR process of small molecules. In this model we consider first the coupling between the excited molecule and the surrounding solvent molecules. We take this coupling and thereby the solvent states to be strongly dependent on the vibrational state of the molecule. After considering this effect, the anharmonic coupling can induce a transition between the molecular vibrations in which the energy mismatch can be compensated by the solvent, because the solvent states are also modified when the vibrational state of the molecule is changed. We present a quantum-mechanical description of the interaction between solute and solvent. The excited molecule and the surrounding solvent molecules are described as one large supermolecule. Using the Born–Oppenheimer approximation the Hamiltonian of this supermolecule has the following form:

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \{R\}^2} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \{I\}^2} + V_{\text{el}}(\{R\}, \{I\}) + V_{\text{anh}}(\{R\}), \quad (1)$$

with $\{R\}$ the set of nuclear coordinates describing the normal modes of the excited molecule and $\{I\}$ all other nuclear coordinates of the supermolecule describing the positions and vibrations of the surrounding solvent molecules. The potential energy $V_{\text{el}}(\{R\}, \{I\})$ is given by $\langle \phi_{\text{el}}(\{r\}, \{R\}, \{I\}) | H_{\text{el}}(\{r\}, \{R\}, \{I\}) | \phi_{\text{el}}(\{r\}, \{R\}, \{I\}) \rangle$, where the integration is carried out over the electron coordinates $\{r\}$. The Hamiltonian H_{el} contains the kinetic energy of the electrons and all the electrostatic interactions between electrons and nuclei.

Although the strong interaction between molecular vibrations and surrounding solvent molecules leads to a strong modification of energies and wave functions, we would like to model this interaction in such a way that it does not lead to direct energy transfer from the excited vibration to the liquid. This can be achieved by employing a second Born–Oppenheimer approximation in which it is assumed that the vibrational wave functions that form the solution of the Hamiltonian $H_{\text{vib}} = (\hbar^2/2m)(\partial^2/\partial \{R\}^2) + V_{\text{el}}(\{R\}, \{I\})$, depend only parametrically on the liquid coordinates $\{I\}$. We obtain a new potential $V_{\text{vib}}(\{I\})$ which is given by $\langle \phi_{\text{vib}}(\{R\}, \{I\}) | H_{\text{vib}}(\{R\}, \{I\}) \times | \phi_{\text{vib}}(\{R\}, \{I\}) \rangle$, where the integration is carried out over the normal mode coordinates $\{R\}$. This second Born–Oppenheimer approximation implies that we assume that the vibrations of the excited molecule can adapt infinitely fast to changes of the relative positions of the surrounding molecules in the liquid.

The vibrational energy that depends on the vibrational state, enters the Hamiltonian in the coordinates $\{I\}$ as a potential energy term. This means that a potential well is formed of which the energy depends on $\{I\}$. Depending on the value of $\{I\}$, more or less vibrational energy will be transferred to liquid kinetic energy, but this amount of transferred energy will remain small compared with the total amount of vibrational energy. In this adiabatic description the vibration will always remain excited and no permanent energy transfer to the liquid can occur. The potential well and thereby the wave functions in $\{I\}$ will strongly depend on the vibrational state of the molecule. The wave function in the nuclear coordinates can now be written as a product of a function describing the vibrational modes of the molecule and a function describing the positions of the molecules in the supermolecule: $\Psi(\{R\}, \{I\}) = \phi_{\text{vib}}(\{R\}, \{I\}) \phi_{\text{liq}}(\{I\})$. The vibrational wave functions and the vibrational energies depend parametrically on the coordinates $\{I\}$.

The terms in the Hamiltonian that violate the second Born–Oppenheimer approximation are proportional to $\langle \phi_{\text{vib},i} | (\partial^2/\partial \{I\}^2) | \phi_{\text{vib},f} \rangle$. These matrix elements contain the kinetic energy operator of the liquid and should be small compared to the vibrational energy for the second Born–Oppenheimer approximation to be valid. Violation of this approximation will lead to decay of the vibrational energy to the continuum of the liquid. In case of excitation of a high-frequency vibration the second Born–

Oppenheimer approximation will be valid. This is confirmed by the observation that an excited high-frequency vibration does not transfer its energy directly to the low-energy degrees of freedom of the surrounding molecules.^{7,8,14,15,17-22} For low-energy vibrations the second Born–Oppenheimer approximation will not be valid because the energy of these vibration can be of the same order as the energy of the liquid. This agrees with the observation that low-energy vibrations transfer their energy directly to the liquid. In polar solvents this direct energy transfer to the solvent can be very fast,³⁰ indicating that the second Born–Oppenheimer approximation is strongly violated.

We describe the rate of excitation of the molecular vibration by substituting the transition dipole moment for ir absorption in Fermi's golden rule,

$$P_{\text{ir}} = \frac{2\pi}{\hbar} \int dE_g |\langle \phi_{\text{vib},i}(\{R\},\{I\}) | \mu(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle \langle \phi_{\text{vib},g}(\{R\},\{I\}) | \phi_{\text{liq},g}(\{I\}) \rangle|^2 \rho(E_i = E_g + h\nu), \quad (2)$$

with g indicating the ground state, i the excited state, and ρ the density of states. In this expression an integration is performed over all the levels $\Psi_g (= \phi_{\text{vib},g} \phi_{\text{liq},g})$ that are occupied before excitation. Equation (2) can be written as follows:

$$P_{\text{ir}} = \frac{2\pi}{\hbar} \int dE_g |\langle \phi_{\text{liq},i}(\{I\}) | \mu(\{I\}) | \phi_{\text{liq},g}(\{I\}) \rangle|^2 \times \rho(E_i = E_g + h\nu), \quad (3)$$

with

$$\mu(\{I\}) = \langle \phi_{\text{vib},i}(\{R\},\{I\}) | \{R\} | \phi_{\text{vib},g}(\{R\},\{I\}) \rangle, \quad (4)$$

where the integration in the equation for $\mu(\{I\})$ is carried out over the normal mode coordinates $\{R\}$. When we assume that for every Ψ_g the absorption band has the same shape, the occupation of the levels Ψ_i is formed by a convolution of the absorption band shape and the occupation of the levels Ψ_g . The width of the absorption band forms a measure for the change of the potential describing the intermolecular interactions upon excitation of a molecular vibration.

In the framework of the second Born–Oppenheimer approximation the IVR process can be described in the following way. The vibrational energy can be calculated as a function of $\{I\}$ taking simultaneously the anharmonic coupling between the unperturbed vibrational levels and the interaction with the solvent molecules into account. This leads to a potential energy surface on which the anharmonic mixing of the vibrational levels will strongly depend on the values of the liquid coordinates $\{I\}$. The anharmonic mixing will attain its maximum value for values of $\{I\}$ for which the uncoupled vibrational levels become degenerate. Excitation with ir light will lead to the production of a wave packet that is localized on a part of this potential energy surface that has strong C–H stretch vibration character. The IVR is represented by the spreading of

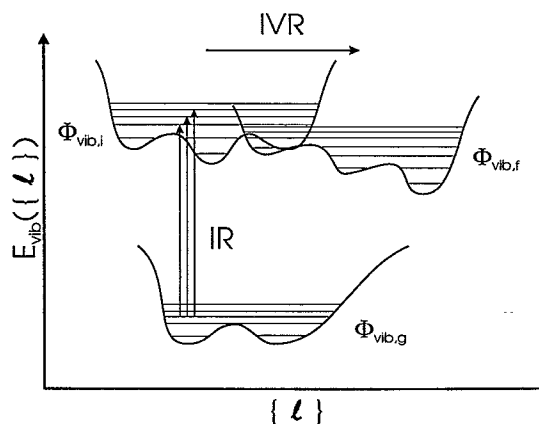


FIG. 1. Description of infrared absorption and intramolecular vibrational relaxation in an adiabatic model. Excitation takes place from a $\phi_{\text{liq},g}$ in the potential of the vibrational ground state to a manifold of $\phi_{\text{liq},i}$ in the excited vibrational state. These states are coupled via anharmonic interactions to $\phi_{\text{liq},f}$ in the potential of the final vibrational states.

this wavepacket over the whole potential energy surface so that eventually all molecular vibrations will contribute to the state of the molecule.

Even using the second Born–Oppenheimer approximation, it is impossible to solve the Hamiltonian with anharmonic interactions and solvent–solute interactions simultaneously. A good approximation of this full theoretical picture of IVR is a description in which first the solute–solvent interaction is taken into account, leading to potential energy curves as a function of $\{I\}$, and second the liquid levels that belong to different vibrational states are coupled by the anharmonic interaction. This model is illustrated in Fig. 1. Using this description, the rate of energy transfer from the levels Ψ_i to the levels Ψ_f is given by the following Fermi's golden rule

$$P_{\text{IVR}} = \frac{2\pi}{\hbar} \int dE_i |\langle \phi_{\text{vib},f}(\{R\},\{I\}) | V_{\text{anh}}(\{R\}) | \phi_{\text{vib},i}(\{R\},\{I\}) \rangle|^2 \times \langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle^2 \rho(E_f = E_i), \quad (5)$$

where we assumed that the anharmonic coupling matrix element $\langle \phi_{\text{vib},f}(\{R\},\{I\}) | V_{\text{anh}}(\{R\}) | \phi_{\text{vib},i}(\{R\},\{I\}) \rangle$ does not depend on $\{I\}$. The compensation of the energy mismatch between the vibrational states $\phi_{\text{vib},i}$ and $\phi_{\text{vib},f}$ is possible because the sets of liquid states $\{\phi_{\text{liq},i}\}$ and $\{\phi_{\text{liq},f}\}$ are different. We can rewrite the Franck–Condon factors $|\langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle|^2$ using the closure condition

$$\begin{aligned} & \langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle \\ &= \int dE_g \langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},g}(\{I\}) \rangle \\ & \times \langle \phi_{\text{liq},g}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle. \end{aligned} \quad (6)$$

This implies that the Franck–Condon factors can be estimated with matrix elements that are strongly related to the

absorption profiles of the transitions from the ground state Ψ_g to the set $\{\Psi_i\}$ and from Ψ_g to the set $\{\Psi_f\}$.

If we define the energy of state Ψ_x equal to $E_{0,x} + E_{\text{liq},x}$ with x equal to g, i, f , and we assume that all levels Ψ_g have the same absorption band to the sets $\{\Psi_i\}$ and $\{\Psi_f\}$, the value of the matrix elements $\langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},g}(\{I\}) \rangle$ and $\langle \phi_{\text{liq},g}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle$ only depends on the energy differences of the liquid energy

$$\langle \phi_{\text{liq},f}(\{I\}) | \phi_{\text{liq},g}(\{I\}) \rangle = F_{f-g}(E_{\text{liq},f} - E_{\text{liq},g}), \quad (7)$$

$$\langle \phi_{\text{liq},g}(\{I\}) | \phi_{\text{liq},i}(\{I\}) \rangle = F_{i-g}^*(E_{\text{liq},i} - E_{\text{liq},g}). \quad (8)$$

If we take $E_{0,i} - E_{0,g}$ and $E_{0,f} - E_{0,g}$ equal to the maxima of the absorption bands, the functions F are equal to the square root of the absorption profiles. If one of the vibrations is not infrared active, the function F can be derived from the isotropic Raman-scattering band.

Using the delta function in the energy in Fermi's golden rule we get $E_{0,i} - E_{0,f} = E_{\text{liq},f} - E_{\text{liq},i}$ and by defining $E = E_{\text{liq},i} - E_{\text{liq},g}$ we obtain the following expression for the rate of IVR:

$$P_{\text{IVR}} = \frac{2\pi}{\hbar} \int dE_i |\langle \phi_{\text{vib},f}(\{R\}, \{I\}) | V_{\text{anh}}(\{R\}) \times | \phi_{\text{vib},i}(\{R\}, \{I\}) \rangle|^2 \int dE F_{i-g}^*(E) F_{f-g}(E_{0,i} - E_{0,f} + E) \Big|_E^2. \quad (9)$$

This expression shows that the rate of IVR is determined by the anharmonic coupling matrix element $\langle \phi_{\text{vib},f}(\{R\}) | V_{\text{anh}}(\{R\}) | \phi_{\text{vib},i}(\{R\}) \rangle$ with the integration carried out over $\{R\}$, the energy difference $E_{0,i} - E_{0,f}$ and the width of the functions F_{i-g}^* and F_{f-g} .

The occupation of the levels Ψ_g does not influence the transition probability because it was assumed that for every Ψ_g the transition probabilities to the sets $\{\Psi_i\}$ and $\{\Psi_f\}$ are equal. In the liquid phase this is not a bad assumption, because the molecules experience all possible liquid surroundings which implies that the occupied liquid levels must be strongly delocalized in $\{I\}$. Due to this delocalization, all Ψ_g will have about the same absorption band to the sets $\{\Psi_i\}$ and $\{\Psi_f\}$. The occupation of delocalized levels for every molecule in the liquid means that every molecule will have the same absorption band so that the transition is homogeneously broadened. Only in this limit the assumption used in Eq. (9) that the functions F are given by the square root of this absorption profile will be valid. When the liquid is frozen to a glass, the surroundings of each molecule becomes fixed indicating that mainly low-energy liquid levels are occupied that are localized in $\{I\}$. These localized liquid levels are in fact glass levels. The state of each supermolecule is then localized in a particular well of the potential energy surface. Due to this localization of the ground-state levels, the absorption bands of different Ψ_g to the sets $\{\Psi_i\}$ and $\{\Psi_f\}$ will be different, mainly due to the fact that the energy at which the transition probability has its maximum depends on the value of

$\{I\}$. Therefore the absorption profile becomes strongly inhomogeneously broadened and Eq. (9) is no longer valid.

In principle, those vibrational states that are strongly mixed by anharmonic interactions will also show the largest rate of IVR. However, there is one important difference between the expression describing the anharmonic mixing of two vibrational states and the golden rule expression (5) for IVR. The first contains a double integral over the liquid level distributions of both vibrational states whereas in the expression for IVR this double integral is reduced to a single one as a result of the delta function in the energy. The consequence is that the amount of anharmonic mixing is mainly determined by the energy that corresponds with the central part of the liquid energy level distribution, whereas the IVR will be determined by the probability in the overlapping wings of the liquid energy level distributions. Therefore, a change in the width of the absorption band due to a change in solvent will have little effect on the anharmonic mixing but can lead to a dramatic increase or decrease of the rate of IVR. Therefore it is not possible to derive the rate of IVR just from the anharmonic mixing that can be obtained from the relative strengths of the absorption bands in the infrared absorption spectrum.

RESULTS

Experimental results, dilute solutions

We investigate the vibrational dynamics after excitation of the C-H stretch vibration of dilute solutions of CHCl_3 , CHBr_3 , and CHI_3 dissolved in CDCl_3 and C_6D_6 . The absorption band of the C-H stretch vibration is only homogeneously broadened on the picosecond time scale at room temperature. Hence in our experiment the whole absorption band will be excited and no spectral hole burning can be observed.⁵ Inhomogeneous broadening effects can only become important on a much shorter (femtosecond) time scale because spectral correlation times are found to be very short in the liquid phase.³¹

Typical results of ir pump-probe measurements are presented in Figs. 2-5. In all figures we observe that when pump and probe overlap, the transmission of the probe is increased due to the saturation of the excitation by the pump. In Figs. (a) the central frequency of the laser pulses is at the high-frequency side of the absorption band whereas in Figs. (b) the central frequency is at the low-frequency side of the absorption band. The figures show that the relaxation takes place via two consecutive relaxation processes. In Figs. (b) we observe an overshoot of the decrease in transmission of the probe. This indicates that the absorption band shifts to lower frequencies after the first relaxation process and comes better into resonance with the spectrum of the probe pulse in Figs. (b) and shifts out of resonance in Figs. (a). The observed shift of approximately $10\text{--}15\text{ cm}^{-1}$ is the result of the first relaxation process in which a large part of the energy is transferred to other vibrations within the excited molecule that are anharmonically coupled to the C-H stretch vibration. The observed overshoot of the decrease in transmission in Figs. (b) cannot be the result of excited-state absorption to the

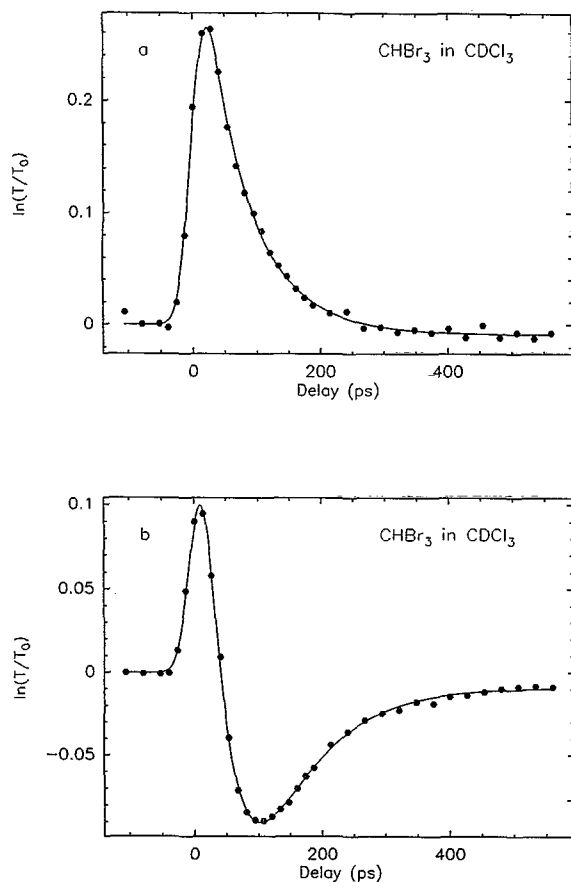


FIG. 2. Relative transmission ($\ln(T/T_0)$) of an infrared probe pulse as a function of the delay between probe and pump pulse for the C–H stretch vibration of a dilute solution of CHBr_3 dissolved in CDCl_3 ($\nu_{\text{max}}=3031 \text{ cm}^{-1}$) for two different central frequencies. The numerical results that are calculated with the time constants of Tables I and II, are represented by the solid curves. (a) 3040 cm^{-1} (b) 3024 cm^{-1} .

first overtone of the C–H stretch vibration because this transition would require a frequency that is $100\text{--}200 \text{ cm}^{-1}$ lower.⁵

We observe that as a result of the second process the transmission rises again indicating that the absorption band shifts back to its original position. In this process the energy is equilibrated over all degrees of freedom and is thus mainly transferred from the molecular vibrations to the surrounding solvent molecules. Hence this process is predominantly an intermolecular energy transfer (IET) process.

For large delay times the transmission of the probe is at a constant level. This level can be somewhat increased or decreased compared to the situation before the pump pulse entered the sample. This increase or decrease reflects how the absorption coefficient changes when the temperature of the sample is raised as a result of the IET process. From the comparison between the temperature dependence of the conventional absorption spectrum and the change of the absorption coefficient for large delay times in the time-resolved measurements, we estimate an average rise of the temperature in the focus of $30 \pm 5 \text{ K}$. The relaxation be-

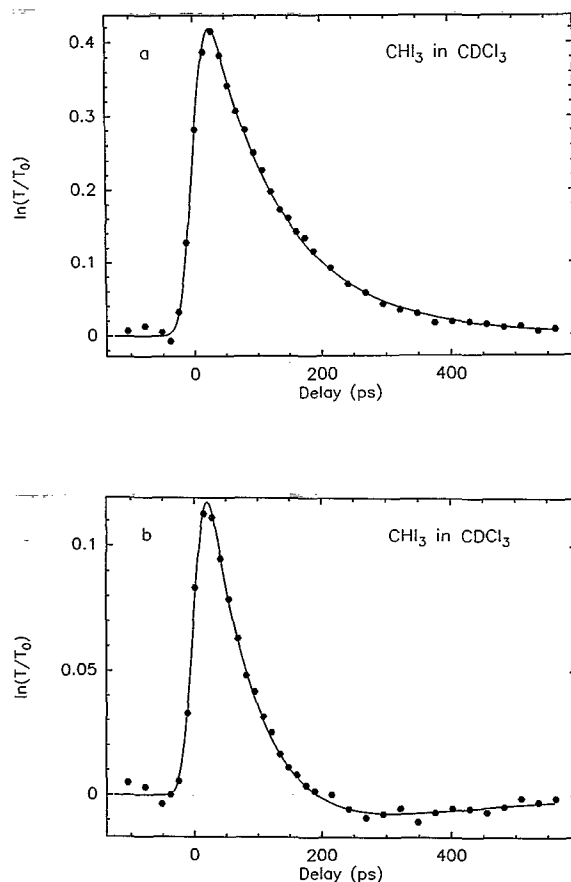


FIG. 3. As Fig. 2 for a dilute solution of CHI_3 dissolved in CDCl_3 ($\nu_{\text{max}}=3014 \text{ cm}^{-1}$). (a) 3016 cm^{-1} (b) 3006 cm^{-1} .

havior is similar to that of CHCl_3 , CHBr_3 , and CHI_3 dissolved in CCl_4 and $\text{C}_3\text{D}_6\text{O}$,^{14,19,20} but the time constants of the two relaxation processes are different.

The time constants of the two relaxation processes can be determined by comparing the experimental results with numerical simulations. These numerical calculations are represented in the figures by solid lines. The amount of absorption of pump and probe can be calculated as a function of their relative delay using a simple kinetic model. In this model the ground and excited state of the C–H stretch with and without excitation of the other molecular vibrations are modeled as single levels. The levels are coupled by the relaxation processes and the transitions induced by the laser pulses. We use as input parameters the pulse widths and intensities of pump and probe pulses and we fit the absorption coefficients and the exponential relaxation time constants. In this model we assume that the combined excitation of the other molecular vibrations as a result of the IVR process can be described as a single change of the absorption coefficient and that the relaxation of this change can be fit with a single exponential. For a specific combination of solute and solvent, the relaxation time constants of the two successive relaxation processes should be independent of the central frequency of the laser pulses. It turns out that indeed for all experiments on a specific so-

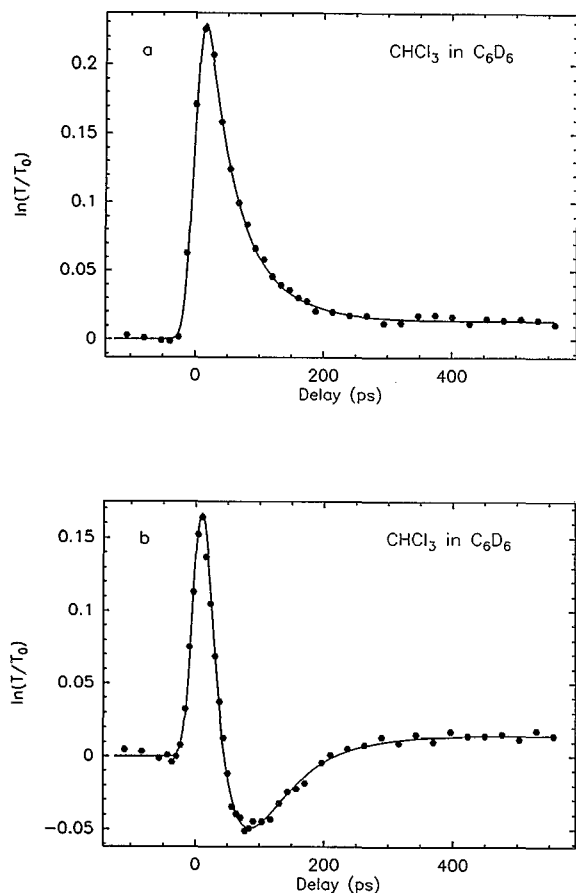


FIG. 4. As Fig. 2 for a dilute solution of CHCl_3 dissolved in C_6D_6 ($\nu_{\text{max}} = 3016 \text{ cm}^{-1}$). (a) 3026 cm^{-1} (b) 3011 cm^{-1} .

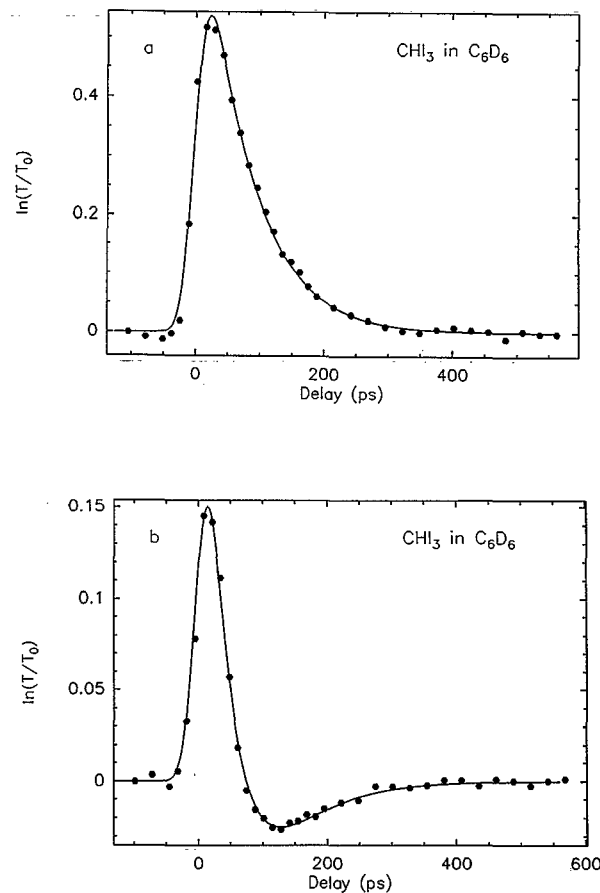


FIG. 5. As Fig. 2 for a dilute solution of CHI_3 dissolved in C_6D_6 ($\nu_{\text{max}} = 3007 \text{ cm}^{-1}$). (a) 3016 cm^{-1} (b) 2995 cm^{-1} .

lution the observed transmission of the probe can be simulated with the same time constants. We observe that the time constants of both IVR and IET, presented in Table I, strongly depend on the specific combination of solute and solvent.

Experimental results, pure liquids

We also investigate the vibrational dynamics of pure CHCl_3 and pure CHBr_3 . For both molecules we observe again that the relaxation takes place via two consecutive relaxation processes. The time constants of these processes are presented in Table I.

For CHCl_3 (Fig. 6), we observe that the transmission level for large delay times is influenced by the central frequency of the laser pulses. This can be explained from the fact that a change in the laser frequency changes the detuning and thereby the amount of absorbed energy. When the frequency is near the maximum of the absorption band the amount of absorbed energy and the temperature rise after the IET process are that large that the CHCl_3 in the focus will strongly expand (CHCl_3 has a low boiling point of 61.7°C at atmospheric pressure³²), so that the medium becomes less dense and the probe will be less well absorbed. Even when the transmission is at a high level for large delay times [Figs. 6(b) and 6(c)], we observe that

the transmission is still very low for short delay times. This indicates that the first relaxation process does not lead to a rise in temperature and therefore this observation forms additional proof for the intramolecular character of the first relaxation process.

For pure CHBr_3 (Fig. 7) we observe that the second relaxation process is exceptionally slow and that the transmission of the probe is at a very low transmission level for large delay times. Although the amount of dissipated energy per molecule is even larger than in the case of pure CHCl_3 , we do not observe boiling of the CHBr_3 after the IET process, presumably because the boiling temperature of CHBr_3 is much higher (149.5°C at atmospheric pressure³²).

Calculated results based on the theoretical model for IVR

With expression (9) we are able to calculate the rate constants for IVR for the different combinations of solute and solvent and the pure liquids. We fitted all measured absorption bands with two Lorentzians, one for the low-frequency side of the absorption band and one for the high-frequency side. The calculation also requires the values of the vibrational anharmonic matrix elements and the energy gaps between the C–H stretch vibration and the combina-

TABLE I. Exponential and theoretical time constants of the relaxation of the haloforms CHCl_3 , CHBr_3 , and CHI_3 after excitation of the C–H stretch vibration. Also presented are the widths of the Lorentzians which are used to fit the absorption band.

	Solvent	Bwl	Bwh	T_{IVR} (exp)	T_{IVR} (the)	T_{IET} (exp)
CHCl_3	pure	16 cm^{-1}	22 cm^{-1}	24 \pm 2 ps	29 \pm 5 ps	120 \pm 5 ps
	CCl_4	14 cm^{-1}	26 cm^{-1}	30 \pm 2 ps	30 ps (ref)	140 \pm 5 ps
	CDCl_3	14 cm^{-1}	20 cm^{-1}	36 \pm 2 ps	36 \pm 6 ps	160 \pm 7 ps
	C_6D_6	24 cm^{-1}	32 cm^{-1}	32 \pm 2 ps	32 \pm 5 ps	62 \pm 4 ps
	$\text{C}_3\text{D}_6\text{O}$	38 cm^{-1}	24 cm^{-1}	6 \pm 1 ps	17 \pm 2 ps	15 \pm 2 ps
CHBr_3	pure	14 cm^{-1}	22 cm^{-1}	28 \pm 2 ps	65 \pm 10 ps	650 \pm 20 ps
	CCl_4	12 cm^{-1}	20 cm^{-1}	56 \pm 2 ps	77 \pm 12 ps	260 \pm 10 ps
	CDCl_3	13 cm^{-1}	21 cm^{-1}	45 \pm 2 ps	71 \pm 12 ps	78 \pm 4 ps
	C_6D_6	14 cm^{-1}	23 cm^{-1}	36 \pm 2 ps	62 \pm 10 ps	30 \pm 3 ps
	$\text{C}_3\text{D}_6\text{O}$	52 cm^{-1}	38 cm^{-1}	5 \pm 1 ps	18 \pm 2 ps	19 \pm 2 ps
CHI_3	CCl_4	20 cm^{-1}	24 cm^{-1}	130 \pm 5 ps	116 \pm 15 ps	260 \pm 10 ps
	CDCl_3	18 cm^{-1}	22 cm^{-1}	140 \pm 5 ps	135 \pm 15 ps	100 \pm 5 ps
	C_6D_6	30 cm^{-1}	30 cm^{-1}	45 \pm 2 ps	72 \pm 12 ps	65 \pm 4 ps
	$\text{C}_3\text{D}_6\text{O}$	36 cm^{-1}	28 cm^{-1}	54 \pm 2 ps	66 \pm 10 ps	<20 ps

tion tones. To be able to calculate these values, we should first know to which combination tones the excited C–H stretch vibration (ν_1) transfers its energy. For molecules in the gas phase, the anharmonically coupled combination tones can be identified from the absorption band shapes.^{33,34} For molecules in the liquid phase, this is not

possible because the absorption bands are strongly broadened as a result of the intermolecular interactions.³⁵

Anharmonic coupling can only take place between combination tones of the same symmetry. It is known that there exists a strong coupling between the C–H stretch vibration and the first overtone of the C–H bend vibration

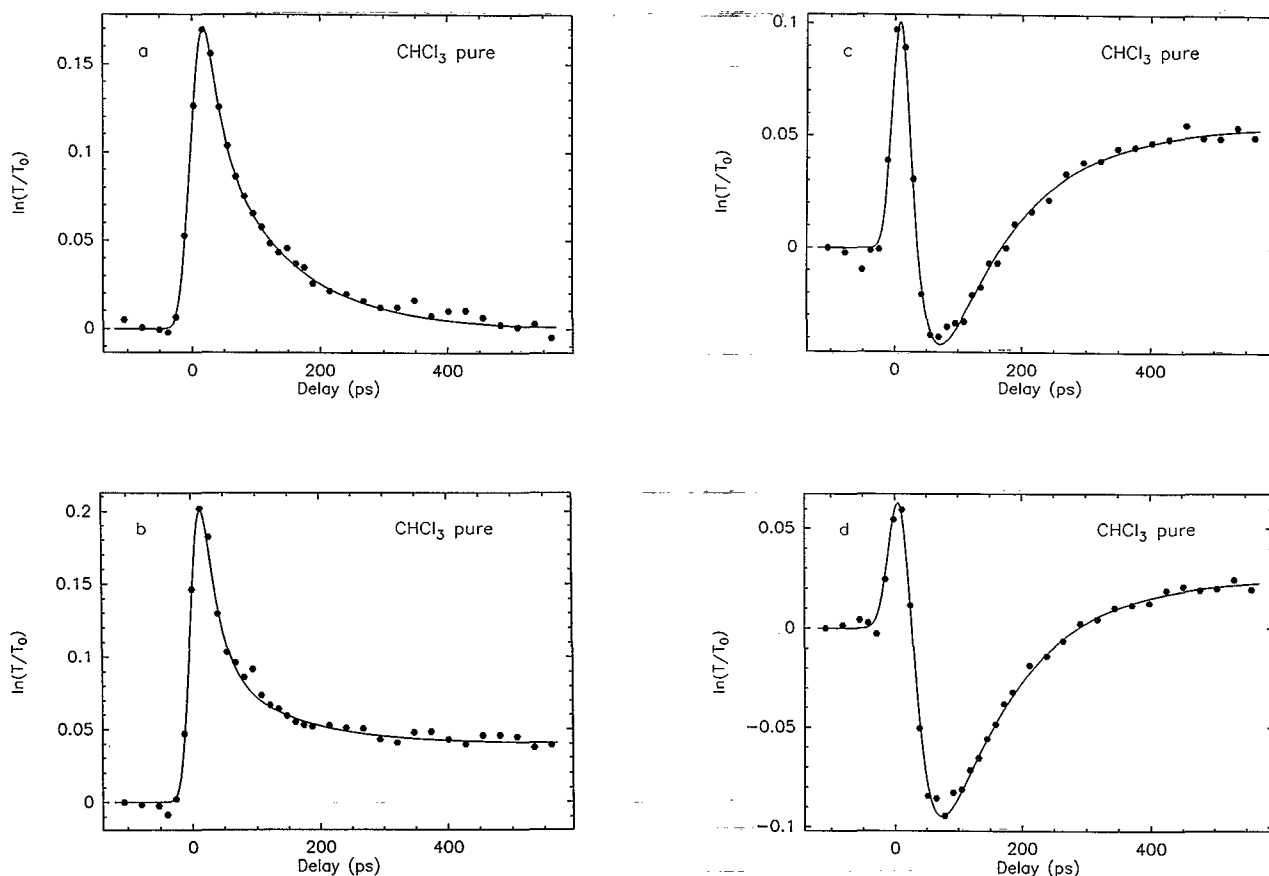


FIG. 6. As Fig. 2 for pure CHCl_3 ($\nu_{\text{max}}=3022 \text{ cm}^{-1}$) for four different central frequencies. (a) 3028 cm^{-1} (b) 3025 cm^{-1} (c) 3019 cm^{-1} (d) 3017 cm^{-1} .

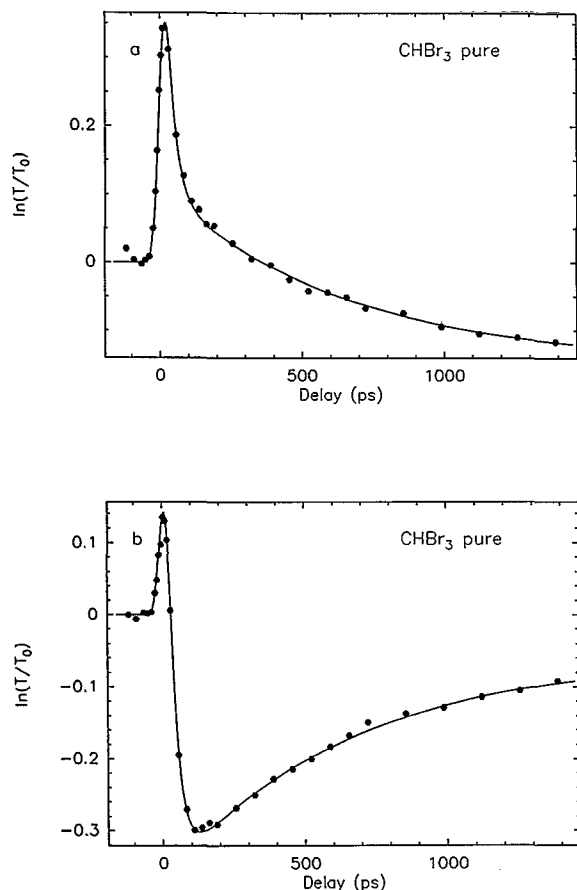


FIG. 7. As Fig. 2 for pure CHBr_3 ($\nu_{\text{max}}=3022 \text{ cm}^{-1}$). (a) 3030 cm^{-1} (b) 3016 cm^{-1} .

(ν_4).³⁶⁻⁴⁰ The symmetries and energies of the molecular vibrations of the haloforms are presented in Table II.⁴¹ It follows from this table that the energy difference between the C-H stretch vibration and the overtone of the C-H bend vibration is still substantial so that direct transfer to this overtone appears to be unlikely. In a previous study on CHBr_3 dissolved in CCl_4 , it was found that the IVR process leads to excitation of the symmetric CBr_3 vibration (ν_2). The combination tone of the overtone of the C-H bend vibration and the symmetric CX_3 stretch vibration comes quite close in energy to the energy of the C-H stretch vibration. Therefore, we suggest that this is the

TABLE II. Character, symmetry, and energies required to excite the first excited state of the molecular vibrations of CHCl_3 , CHBr_3 , and CHI_3 . The characters s and d denote symmetric and degenerate, respectively.

Vibration	Character	Symmetry	CHCl_3	CHBr_3	CHI_3
ν_1	C-H s-stretch	A_1	3021 cm^{-1}	3032 cm^{-1}	3013 cm^{-1}
ν_2	CX_3 s-stretch	A_1	680 cm^{-1}	541 cm^{-1}	425 cm^{-1}
ν_3	CX_3 s-deform	A_1	363 cm^{-1}	222 cm^{-1}	154 cm^{-1}
ν_4	C-H d-bend	E	1220 cm^{-1}	1149 cm^{-1}	1068 cm^{-1}
ν_5	CX_3 d-stretch	E	774 cm^{-1}	669 cm^{-1}	578 cm^{-1}
ν_6	CX_3 d-deform	E	261 cm^{-1}	155 cm^{-1}	110 cm^{-1}

most important combination tone to which energy is transferred in the IVR process. This implies that the coupling potential energy term V_{anh} should be proportional to $R_1 R_4^2 R_2$ with R_x denoting the normal coordinate of vibration ν_x . When we assume that the vibrational wave functions are harmonic, then the matrix element $\langle \phi_{\text{vib},f} | V_{\text{anh}} | \phi_{\text{vib},i} \rangle$ is proportional to $\langle \phi(2\nu_4 + \nu_2) | R_1 R_4^2 R_2 | \phi(\nu_1) \rangle = \hbar^2 / (2\sqrt{2} \sqrt{m_1 \omega_1 m_4 \omega_4} \sqrt{m_2 \omega_2})$, with m_x the reduced mass and ω_x the frequency belonging to normal mode x . We take equal values for the reduced masses of the C-H stretch (ν_1) and the C-H bend vibration (ν_4) for the three haloforms. The reduced mass of the ν_2 vibration depends on the mass of the halogen atoms and increases going from CHCl_3 to CHBr_3 to CHI_3 . The frequencies are obtained from Table II. We calculate the rate constants for the IVR for the different combinations of solute and solvent and the pure liquids taking the experimental rate constant of 30 ps for the IVR of CHCl_3 dissolved in CCl_4 as a reference. In Table I the calculated rate constants for the IVR are presented together with the experimentally determined rate constants and the widths of the Lorentzians that we used to fit the absorption bands. In our calculation we used the same shape of the absorption band for the combination tone as for the C-H stretch vibration.

DISCUSSION

Dilute solutions

The results of Table I show that most calculated rate constants for the IVR for the dilute solutions are in good agreement with the experimentally determined rate constants. The trends we observe in the experimental results are well reproduced by the theoretical results.

We observe that the rate of IVR decreases going from CHCl_3 to CHBr_3 to CHI_3 for all solvents. From our model we deduce that this is mainly caused by the fact that the energy gap between the excited ν_1 vibration and the proposed combination tone $2\nu_4 + \nu_2$ increases. The observed decrease in the rate of IVR cannot be due to a change in the width of the absorption bands of the haloforms, because in a particular solvent these bands are approximately equally broad for the three haloforms. It is also not the result of a change in the vibrational anharmonic matrix element since this would lead to the opposite effect.

We also observe that the rate of IVR increases with increasing absorption band width. A broad absorption band indicates a strong interaction between solute and solvent molecules. In the theoretical model it was shown that the change of the intermolecular interactions upon a change of the vibrational state leads to a modification of the liquid wave functions. This allows the transfer of energy between the excited molecule and the liquid in the transition so that the energy mismatches between ν_1 and the coupled combination tone can be compensated. Therefore the rate of IVR in the solvents C_6D_6 and $\text{C}_3\text{D}_6\text{O}$ will be faster than in CCl_4 and CDCl_3 because the interactions between the haloforms and C_6D_6 and $\text{C}_3\text{D}_6\text{O}$ are very strong due to their large electronic polarizability and large

dipole moment respectively. In the case of C_3D_6O the experimental rate constants are smaller than the calculated ones. A possible explanation for this observation is that due to the very broad absorption profiles of the haloforms dissolved in C_3D_6O , other combination tones like $2\nu_4$ can also significantly contribute to the IVR process.

After the energy of the excited C–H stretch vibration is transferred to lower-energy vibrations we observe that these vibrations transfer their energy to the solvent in the IET process. This implies that for these lower-energy vibrations the second Born–Oppenheimer approximation that was used in the description of the IVR process is no longer valid. The IET process can be modeled by describing the interaction between solute and solvent by means of molecular dynamics simulations.^{42,43} The rate of energy transfer to the solvent will be both determined by the frequency match between the solvent and the solute modes and the strength of the coupling between these modes. This coupling will increase with increasing electrostatic interaction between solute and solvent. Most of the experimentally observed trends in the rate of the IET process can be well explained from the strength of the interaction between solute and solvent. If there is very little interaction with the solvent, as in CCl_4 , the IET process is much slower for $CHBr_3$ and CHI_3 than for $CHCl_3$. When CCl_4 is replaced by a solvent that has much more electrostatic interaction with the haloform molecules we observe that the IET process is much more accelerated for $CHBr_3$ and CHI_3 than for $CHCl_3$. These results suggest that the electrical polarizability of the halogen atoms of the haloform molecules is an important parameter for this rate. The relatively fast IET of $CHBr_3$ and CHI_3 dissolved in $CDCl_3$, C_6D_6 and C_3D_6O can therefore be explained from the strong dipole-induced dipole and induced dipole–induced dipole interactions at the halogen atom side of the haloform molecule.

For almost all combinations of solute and solvent the relaxation can be very well described by an IVR process followed by an IET process. Only for CHI_3 dissolved in C_3D_6O no transient shift of the absorption band can be observed and only one relaxation time constant is observed. In a previous study on the relaxation of a high-energy vibration of N_3^- dissolved in strongly polar (protic) solvents also only one relaxation time constant could be observed.⁴⁴ These observations raise the question whether it is possible that a high-energy vibration in a polyatomic molecule directly transfers its energy to the solvent instead of relaxing via IVR. In principle this relaxation behavior can still be explained with a mechanism in which the IET follows the IVR. When the IET process is much faster than the IVR process no accumulation of molecules with a shifted absorption band takes place so that only the time constant of the IVR process can be observed. For CHI_3 the IVR will indeed be slow as a result of the large energy gap between ν_1 and $2\nu_4 + \nu_2$ whereas the IET will be fast due to the strong coupling of the polarizable iodine atoms with the dipole moment of the solvent. This mechanism could also apply for N_3^- dissolved in protic solvents.⁴⁴ However, it can not be excluded that the excited high-energy vibration directly transfers its energy to the solvent. In that case

no temporal excitation of other intramolecular vibrations occurs and the measured relaxation time constant is that of a direct IET process from the excited vibration to the solvent. This mechanism requires that the frequencies of the solvent are high enough to allow a direct energy transfer to the solvent which is possible if the solvent is strongly polar.

Pure liquids

If we compare the experimental time constants of the relaxation processes of $CHCl_3$ dissolved in $CDCl_3$ (36 ± 2 and 160 ± 7 ps) with those of pure $CHCl_3$ (24 ± 2 and 120 ± 5 ps) the time constants of the latter are somewhat shorter. This might be caused by the fact that the amount of dissipated energy per molecule is larger for pure $CHCl_3$ than for a dilute solution of $CHCl_3$ dissolved in $CDCl_3$. Therefore the pure $CHCl_3$ sample will experience a larger rise in temperature during the experiment. In our calculation of the IVR rate we assumed that the absorption band does not depend on temperature. However, at higher temperatures, liquid levels with higher energies will be occupied that likely have broader absorption bands. From the theoretical model it follows that liquid levels with broader absorption bands can compensate larger energy mismatches in the vibrational energy transfer. Therefore, the occupation of these levels will lead to faster relaxation processes.

For pure $CHBr_3$ we observe that the IVR process is much faster (28 ± 2 ps) than for a dilute solution of $CHBr_3$ in CCl_4 (56 ± 2 ps) and for a dilute solution of $CHBr_3$ in $CDCl_3$ (45 ± 2 ps). This is probably caused by the same temperature effect we described for pure $CHCl_3$. This temperature effect will be even stronger as a result of the high absorption coefficient of $CHBr_3$.

In contrast, the IET process of pure $CHBr_3$ is very slow (650 ps) compared to that of dilute solutions of $CHBr_3$ and pure $CHCl_3$. In addition, the transmission of the probe is at a strongly decreased transmission level for large delay times. In this respect there are two important differences between $CHBr_3$ and $CHCl_3$. First, due to the high absorption coefficient of $CHBr_3$ the concentration of excited molecules is larger in pure $CHBr_3$ than in pure $CHCl_3$. Second, the molecular vibrations involving halogen atoms have much lower energies in $CHBr_3$ than in $CHCl_3$. Therefore a possible explanation for the slow IET process is that a very high concentration of excited molecules have to transfer their energy to a limited number of lower-degrees of freedom (translational, rotational). These other degrees of freedom will get highly excited and may reexcite molecular vibrations of the $CHBr_3$ molecules. Hence, the energy will remain stored in low-lying vibrations that induce shifts of the absorption band of the C–H stretch vibration so that the observed shift of the absorption band relaxes very slow. After this relaxation the level of transmission is still strongly decreased irrespective whether the central frequency of the laser pulses is below or above the maximum of the absorption band. This indicates that after the IET process there are still degrees of freedom occupied that increase the absorption coefficient of the C–H stretch vibration.

CONCLUSIONS

The relaxation of the excited C–H stretch vibration of dilute solutions of CHCl_3 , CHBr_3 , and CHI_3 dissolved in CCl_4 , CDCl_3 , C_6D_6 , and $\text{C}_3\text{D}_6\text{O}$ and of the pure liquids CHCl_3 and CHBr_3 takes place via two consecutive relaxation processes. The first process is mainly an intramolecular vibrational relaxation (IVR) process, which leads to a shift of the absorption band of the C–H stretch vibration to lower frequencies. The second process is mainly an intermolecular energy transfer (IET) process, in which the energy is equilibrated over all degrees of freedom, leading to a relaxation of the shift.

We developed a new theoretical model in which the effects of the strong coupling between molecular vibrations and surrounding solvent molecules on the rate of IVR are considered. In this model the solvent can compensate for the energy mismatches between the excited vibration and the anharmonically coupled combination tones, although the anharmonic coupling does not depend explicitly on the solvent coordinates. With this model we can calculate the rate constants of the IVR process for the haloforms dissolved in the different solvents. From the comparison of the experimental and the theoretical results we deduce that the decrease in IVR rate going from CHCl_3 to CHBr_3 to CHI_3 is mainly due to the increase of the energy mismatch between the excited C–H stretch vibration and anharmonically coupled combination tones.

We also deduce that the observed increase of the rate of IVR in the solvents C_6D_6 and $\text{C}_3\text{D}_6\text{O}$ compared to CCl_4 and CDCl_3 is due to the fact that strong electrostatic interactions between solute and solvent allow large changes in the energy of the liquid when the vibrational state is changed.

The rate of IET of CHBr_3 and CHI_3 is strongly accelerated when the electrostatic interaction with the solvent molecules increases. For CHCl_3 this effect is much smaller. These results suggest that the electrical polarizability of the halogen atoms of the haloforms is a very important parameter for the rate of the IET process.

We observe that for pure CHCl_3 and for pure CHBr_3 the rate of IVR is faster than for dilute solutions of CHCl_3 and CHBr_3 in solvents of equal polarity. This effect is most likely due to the large amount of absorbed energy per molecule in the pure liquids. Finally we find that the rate of IET is very slow for pure CHBr_3 , probably as a result of the saturation of the energy transfer to the low-energy degrees of freedom of the liquid.

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