Ultrafast redistribution of vibrational energy in liquids
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Observation of a Bottleneck in the Vibrational Relaxation of Liquid Bromoform

We present a study on the vibrational dynamics of the C–H stretch vibration of bromoform (CHBr₃) in the pure liquid using picosecond mid-infrared pump-probe spectroscopy. Delay scans and transient spectra confirmed earlier results that relaxation occurs via an intermediate level, which causes a transient redshift of the C–H stretch frequency. We determined this redshift to be 17 cm⁻¹ and identified the intermediate level with the singly excited C–H bend mode. We observed that relaxation from the intermediate level is exceptionally slow and non-exponential. These observations suggest the presence of a "bottleneck" in the relaxation. The occupation of a long-living "bottleneck" level may also be responsible for the observation of a long-living absorption around 3022 cm⁻¹.

5.1 Introduction

In the past decades there have been many time-resolved studies on the vibrational dynamics of small molecules in the electronic ground state. These studies generally use intense infrared laser pulses to excite a molecular vibration and use either anti-Stokes Raman scattering⁴⁷ or induced infrared transmission changes⁴ to monitor the decay of the excitation. In many time-resolved studies, the excitation of a high-frequency molecular vibration is observed to relax via two consecutive steps. see References 8, 15, 17, 18, 19, 85, 86, 87, 89, 90, 91, 93, 107, 111, 163, 202, 211, and 215. In a first step, energy is transferred from the excited vibration to a few selected other vibrational modes in the molecule. The excitation of these accepting modes often causes a shift of the absorption band of the vibration that was originally excited, because of anharmonic coupling. In a second step, the energy is equilibrated over all degrees of freedom, implying that the energy is redistributed over all other modes of the molecule, the modes of nearby molecules and intermolecular degrees of freedom.

The exact nature of the intermediate state is usually not well known, although likely candidates are often suggested in the form of (combinations of) low-frequency vibrations. There are only a few studies in which the intermediate state could be identified. For instance, in a recent study on the vibrational dynamics of liquid chloroform (CHCl₃),⁹³ it was found that the relaxation of the C–H stretch mode leads to a transient population of the C–H bend and C–Cl stretch modes.

Earlier studies on the vibrational dynamics of bromoform (CHBr₃), see References 15, 17, 85, 86, 87, and 90, also indicated the presence of an intermediate state in the relaxation of the C–H stretch mode. In these studies, a bi-exponential decay and a transient redshift of the C–H stretch absorption band were observed. However, the exact nature of the inter-
mediate state has remained unknown: One or more of the other vibrations of the CHBr₃ molecule are assumed to cause the redshift. Whether one mode or a combination of modes are excited with one or more vibrational quanta has not yet been determined. It is also unclear whether relaxation from the intermediate state involves one or more vibrational quanta.

Here we present a detailed investigation of the vibrational dynamics of CHBr₃ using two-colour mid-infrared pump-probe spectroscopy. We find strong evidence that the relaxation of the intermediate state does not lead to a full thermalisation, but encounters a vibrational “bottleneck”.

5.2 EXPERIMENT

The experimental set-up to generate intense, tunable mid-infrared pulses is depicted schematically in Figure 5.1. The pump pulses for the parametric down-conversion process are provided by an actively and passively mode-locked Nd:YAG laser (Quantel YG502C). This laser delivers pulses of 34 ps (FWHM) with a wavelength of 1064.1 nm, an energy up to 60 mJ and a repetition rate of 10 Hz. An autocorrelation trace of these pulses can be found in Section 7.2. These pulses are used to pump two identical OPG/OPA stages, based on three 5 cm long lithium niobate (LiNbO₃) crystals each (optical axis cut at 47.1°). In each branch, the first crystal is pumped with 5 mJ 1064.1 nm pulses. The parametrically generated signal and idler pulses are amplified in the second crystal with the remaining part of the pump energy. After the second crystal the idler and pump are reflected out of the beam. The signal pulses (~18 μJ), are used as a seed in a second OPA process in the third crystal, where they are combined collinearly with 8 mJ of 1064.1 nm light. After the third crystal, the signal and pump pulses are reflected out of the beam, yielding idler pulses continuously tunable from approximately 2.1-4.1 μm (~4580–2030 cm⁻¹) and a typical energy of 250 μJ. From a cross-correlation trace of idler pulses from each branch, generated through sum-frequency generation in a 5 mm lithium iodate (LiIO₃) crystal, the pulse duration was determined to be 21 ps, see Figure 5.2. Typical spectra of signal and idler pulses generated in this set-up can be found in Section 7.2.

The pump-probe set-up for picosecond two-colour experiments is shown in Figure 5.3. The idler beam of one OPG/OPA branch is used as a pump, the other is used as a probe. A low intensity probe pulse is split off the relatively intense beam by a broadband infrared beam splitter which reflects about 15%. The transmitted high intensity part (85%) of the
Figure 5.2. Cross-correlation trace of the idler pulses with a frequency of 3316 cm$^{-1}$. The solid line is a Gaussian with a FWHM of 29.9 ps, corresponding to a pulse duration of 21.1 ps (FWHM).

Figure 5.3. Two-colour pump-probe set-up used in the experiments described in this chapter. Legend: BS: beam splitter.
pulse is used as a reference beam. The pump and probe pulses are focused into the sample by a calcium fluoride (CaF₂) lens (focal length 100 mm) with an estimated diameter of the focus of approximately 300 μm. The probe pulses can be delayed with respect to the pump pulses by means of a variable delay (a gold-coated retro-reflector on a translation stage).

This set-up differs from the general description of a pump-probe set-up given in Section 2.2: The reference beam is slightly focused into the sample by a second CaF₂ lens and the intensity is measured by a reference detector to take into account not only the pulse-to-pulse intensity fluctuations, but also the spectral fluctuations of the probe pulses. Because the probe pulses in this picosecond set-up are far from bandwidth-limited, spectral fluctuations can be large. When the absorption band is relatively narrow, as is the case with the C–H stretch absorption of CHBr₃, or when the edge of the band is probed, these spectral fluctuations can have a large influence on the transmission. By sending the reference beam through the sample as well, the effect of the spectral fluctuations can be taken into account. The intensity of the transmitted probe pulses and of the reference pulses are measured by lead selenide (PbSe) photoconductive cells. The pump beam is chopped at 5 Hz to block every other pump pulse to monitor both the intensities of the probe pulse with and without the presence of a pump pulse. This set-up can be used for (quasi) one- or two-colour delay scans or to record transient spectra at a fixed delay between the pump and the probe pulses. The experiments are performed on pure CHBr₃, using a sample length of 50 μm.

5.3 Results and discussion

In all experiments the frequency of the pump pulses was tuned to the C–H stretch frequency of pure CHBr₃ at 3022 cm⁻¹. We measured transient spectra of pure CHBr₃ at various delay times. Three spectra at (relatively) short delay times are shown in Figure 5.4 and four spectra at longer delay times are shown in Figure 5.5. As can be seen in Figure 5.4, an induced absorption starts to appear around 2890 cm⁻¹ during excitation. With increasing delay this absorption decreases, while another induced absorption, centred at 3005 cm⁻¹, increases. We identify the absorption around 2890 cm⁻¹ with the ν = 1 → ν = 2 transition of the C–H stretch vibration, which is at its maximum right after excitation and decays with a decay time constant of about 43 ps. The 1 → 2 transition of the C–H stretch vibration is red-shifted from the 0 → 1 transition, due to the anharmonicity of the C–H stretch mode. At 133 ps, the 1 → 2 absorption has almost completely disappeared, as has the bleaching signal at the position of the 0 → 1 transition. The maximum of the bleaching signal appears to shift to the blue, but this is because at 17 ps, there is almost no absorption around 3005 cm⁻¹, whereas at 40 ps, the absorption at 3005 cm⁻¹ is strong and competes with the red side of the bleaching. The absorption centred at 3005 cm⁻¹ is attributed to the absorption by molecules in an intermediate state |o⁺⟩, which is populated when relaxation from the ν = 1 state occurs. This |o⁺⟩ state will most likely be a state in which one of the other vibrational modes is excited, thereby inducing an anharmonic shift of the C–H stretch frequency. Apparently the cross section of the C–H stretch vibration increases when relaxation to the intermediate state |o⁺⟩ occurs. From Figure 5.5 it is clear that the relaxation from the |o⁺⟩ state is very slow. At longer delay times the absorption starting from the |o⁺⟩ state starts to disappear, while another induced absorption simultaneously appears around 3022 cm⁻¹. This implies that the energy transfer to low-frequency modes of CHBr₃ leads
Figure 5.4. Transient spectra at short delay times. Pump frequency tuned to 3022 cm$^{-1}$. The solid lines are guides to the eye and are fitted to the data, assuming asymmetric Lorentzians for the different line shapes.

to an increased cross section of the C–H stretch vibration and to a negligible anharmonic shift.

From these transient spectra we can determine the anharmonic redshift of the frequency of the absorption starting from the $|0^*\rangle$ state, being 17 cm$^{-1}$ with respect to the C–H stretch frequency. The transient spectra at large delays also give insight in the character of the $|0^*\rangle$ state. We note that the spectra in Figure 5.5 have an “isosbestic” point around 3019 cm$^{-1}$: at this frequency the induced absorption hardly changes when the second relaxation process takes place, which implies that the absorption of the $|0^*\rangle$ does not show a gradual shift during this relaxation. This suggests that the relaxation of the mode responsible for the anharmonic shift only involves one single quantum of vibrational energy. If the intermediate state $|0^*\rangle$ had been a highly excited vibrational state, a stepwise, more gradual decay of the redshift would have been expected. The C–H bend vibration is a very likely candidate, since a strong coupling is known to exist between the C–H stretch vibration and the first overtone of the C–H bend vibration, see References 63, 72, 79, 80, 94, 127, 137, and 179. Furthermore, in a recent study on the vibrational relaxation of liquid CHCl$_3$ by incoherent anti-Stokes Raman scattering, one relaxing C–H stretch quantum was found to produce one C–H bend quantum.\textsuperscript{93} For the present data it can be concluded that the same relaxation mechanism applies to liquid bromoform. Another indication that the $|0^*\rangle$ state involves the C–H bend mode is given by estimates for the anharmonic redshifts of the $\nu_1 \rightarrow \nu_1 + \nu_1$ transition, where $\nu_1$ indicates one vibrational quantum in the C–H stretch mode and $\nu_1$ one of the other modes of the CHBr$_3$ molecule. These redshifts were reported to be:\textsuperscript{78,85} 25 cm$^{-1}$ for $\nu_4$ (C–H bend), 4 cm$^{-1}$ for $\nu_2$ (C–Br$_3$ s-stretch), 3 cm$^{-1}$ for $\nu_3$ (C–Br$_3$ d-stretch) and about 1 cm$^{-1}$ for $\nu_1$ (C–Br$_3$ s-deform) or $\nu_6$ (C–Br$_3$ d-deform). As
we concluded that the second relaxation involves one single vibrational quantum, the only candidate for the mode which causes the observed anharmonic shift is the $\nu_4$, because for the other modes to produce the observed redshift, would require several quanta of these modes. It would still be possible for the other modes to be populated, but since the anharmonic shifts they cause are only a few cm$^{-1}$, they will not have an observable effect in our experiments. It is thus concluded that the relaxation of the induced absorption at 3005 cm$^{-1}$ represents the relaxation of the C–H bend mode.

The observation of a two-step relaxation process agrees with the observations in earlier one-colour experiments on the pure liquid. In order to determine the decay-time constants accurately, we also performed pump-probe delay scans, measured at four probe frequencies, as shown in Figure 5.6. With the pump frequency tuned to 3022 cm$^{-1}$, the probe frequency was tuned to 3023 cm$^{-1}$ to perform a quasi one-colour experiment and to the red (3000 cm$^{-1}$ and 3016 cm$^{-1}$) side of the $0 \rightarrow 1$ transition. Furthermore, the probe was tuned to the frequency of the $1 \rightarrow 2$ transition (2900 cm$^{-1}$). The solid curves in this figure are calculated with a kinetic model, which is illustrated in Figure 5.8 and has been described in detail in Section 3.4 and elsewhere. In this model, the relaxation of the excited vibration $|1\rangle$ occurs via an intermediate state $|\sigma^*\rangle$, rather than directly back to the ground state $|0\rangle$. The rate of relaxation from the first excited state $|1\rangle$ to the intermediate state $|\sigma^*\rangle$ is given by $k_A$ and the relaxation rate of the second step in the relaxation $|\sigma^*\rangle \rightarrow |0\rangle$ is given by $k_B$. The cross section of the $0 \rightarrow 1$ transition is denoted by $\sigma$ and the cross section of the $\sigma^* \rightarrow 1^*$ transition by $\sigma^*$. As discussed above, the centre frequency of the $\sigma^* \rightarrow 1^*$ transition is redshifted by 17 cm$^{-1}$ with respect to the $0 \rightarrow 1$ transition, due to the anharmonic coupling between the C–H bend and C–H stretch modes. Therefore,
Figure 5.6. Two-colour pump-probe delay scans of pure CHBr₃. Pump frequency tuned to 3022 cm⁻¹. The solid lines are calculated using the model described in Section 5.3.
the cross section is different for each probe frequency.

If the frequency of the probe pulse is tuned to the $1 \rightarrow 2$ transition, the decay of the pump-induced absorption change $\Delta \alpha_{12}$ will only depend on the decay of $n_1$, since $n_2 = \infty$:

$$\Delta \alpha_{12} \propto \sigma_{12} n_1(t) = \sigma_{12} n_1(\infty) e^{-k_{1,t}t}$$

and therefore $k_A$ can be determined separately from $k_B$ and the ratio $\sigma^*/\sigma$, contrary to, for example, the experiments described in Chapter 3, because in those one-colour experiments the frequency of the probe pulses could not be tuned separately from the frequency of the pump pulses.

From the data with the probe frequency tuned to the $1 \rightarrow 2$ transition we determined the lifetime $T_1 = 1/k_A$, to be $43 \pm 1$ ps. This value of the decay time for the first relaxation process ($1 \rightarrow \sigma^*$) agrees with the one determined by anti-Stokes Raman scattering.\textsuperscript{87} $40 \pm 4$ ps. Using a value for $k_A$ corresponding to $T_1 = 43 \pm 1$ ps, we tried to fit the data for the other probe frequencies. Especially at a probe frequency of $3000$ cm$^{-1}$, the data could not be accurately fitted, when we described the second relaxation process by an exponential decay. As can be clearly seen in Figure 5.7, the decay from the $|\sigma^*\rangle$ state is non-exponential. The decay from the intermediate level is faster than an exponential decay at first, but then slows down.

In addition, the relaxation from the $|\sigma^*\rangle$ state is observed to be much slower for the pure liquid than for dilute solutions of CHBr$_3$. It is also observed that when the solvent fraction becomes smaller, the relaxation rate from the $|\sigma^*\rangle$ state dramatically decreases.\textsuperscript{15,47,90} These observations strongly suggest that molecules in the $|\sigma^*\rangle$ state decay to another intermediate state, which acts as a "bottleneck": relaxation from this bottleneck state $|b\rangle$ is extremely slow and after some time becomes the so-called rate-limiting step in the relaxation mechanism. This implies that relaxation from the $|\sigma^*\rangle$ state to the $|b\rangle$ state can initially be exponential, but after some time population accumulates in the bottleneck state and thus the relaxation
from the $|\sigma^+\rangle$ state slows down. In view of the absence of an anharmonic shift, the bottleneck state is probably some low-energy mode of the CHBr$_3$ molecule, e.g. the C=Br, s- or d-stretch modes.

In ultrasonic dispersion measurements on pure CHBr$_3$, a relaxation time constant of 2 ns was observed. In a previous study on concentrated solutions of CHBr$_3$, it was argued that the relaxation time constant for ultrasonic dispersion measurements should be related to the one found in pump-probe experiments by a Boltzmann factor. However, this argument is not correct and the lifetime of 2 ns is indeed the lifetime of a long-living vibrational mode in pure CHBr$_3$. Interestingly, similar ultrasonic dispersion measurements on CHCl$_3$ yielded a relaxation time which is nearly 8 times smaller. Previous time-resolved studies on pure CHCl$_3$, see References 15 and 93, also showed that the relaxation in pure CHCl$_3$ is much faster than in pure CHBr$_3$.

Apparently, energy from this bottleneck level cannot be easily transferred to other (low-frequency) modes of the same or neighbouring CHBr$_3$ molecules. In solutions, there are more (solvent) modes available for the energy to be transferred to and therefore the bottleneck level can rapidly decay (and thus no longer forms a bottleneck) or decay via the bottleneck level will not be the only available decay channel; this will result in a faster vibrational decay.

We observed a persistent induced absorption around 3022 cm$^{-1}$ at long delay times, which is even present at a delay of 4.7 ns. In order to investigate whether this absorption might be caused by heating effects, we have studied the temperature dependence of the linear absorption spectrum of the same sample. There we have found that with increasing temperature, there is a blue-shift of the central absorption frequency of about 0.05 cm$^{-1}$ K$^{-1}$ and a relative decrease of the absorbance of about 0.007 K$^{-1}$ between room temperature and 363 K. This decrease of the absorbance includes the volume expansion effect. A typical value for the relative decrease by pure volume expansion is only 0.001 K$^{-1}$ for organic liquids. Hence, even if the volume would not expand at all after relaxation, an absorption decrease is expected, instead of the observed increase. This forms additional evidence that the relaxation of the intermediate state does not lead to a full thermalisation, but rather leads to the occupation of a specific, long-living bottleneck state. For CHBr$_3$ dissolved in carbon tetrachloride (CCl$_4$), we have found a persistent bleaching instead of an induced absorption, even at a very high concentration of 25 vol%. This same bleaching is also found in earlier studies on solutions of this concentration. Apparently, in solution a rapid thermalisation occurs because the energy of the intermediate state can be transferred to modes of the solvent molecules.

Introduction of a bottleneck state in our model requires changes in the rate-equations, and therefore we replace Equation (3.4) with:

$$\frac{dn_{\sigma^+}}{dt} = k_A n_i - k_B (n_{\sigma^+} - c n_b),$$  \hfill (5.2)

and we add an equation for population $n_b$ of the bottleneck level:

$$\frac{dn_b}{dt} = -k_c n_b + k_B (n_{\sigma^+} - c n_b),$$  \hfill (5.3)

where $k_c$ is the relaxation rate from the bottleneck level and $c$ a dimensionless constant.
With this model (see Figure 5.8) we could describe the data obtained at a probe frequency of 3000 cm$^{-1}$, taking $\sigma^*/\sigma \gg 1$, $c = 0.55$, and values for $k_B$ and $k_C$ corresponding to decay times of $1/k_B = 425$ ps and $1/k_C = 833$ ps, respectively. With these values we could also describe the data at the probe frequencies of 3016 cm$^{-1}$ and 3023 cm$^{-1}$. We obtained values for $\sigma^*/\sigma$ of 1.4 and 0.45 at these respective probe frequencies.

In an earlier pump-probe experiment on pure liquid CHBr$_3$, the time constant of the first relaxation process ($1 \rightarrow \sigma^*$) was determined to be $28 \pm 2$ ps, which is clearly too short. This value was determined by one-colour pump-probe experiments, which prohibited the independent determination of $k_A$, as was possible in the two-colour experiments described here. The large error in the previous determination of $k_A$ is mainly due to the fact that the relaxation from the $|\sigma^*\rangle$ state was assumed to be exponential, which is clearly not the case, as we have shown here.

5.4 Conclusions

Relaxation of the excited C–H stretch vibration of CHBr$_3$ in the pure liquid occurs in at least three consecutive steps. In the first step vibrational energy is transferred with a time constant of $43 \pm 1$ ps from the $v = 1$ state of the C–H stretch vibration to an intermediate state $|\sigma^*\rangle$. From the transient spectra it is clear that the intermediate state is another molecular vibration of CHBr$_3$ which is singly excited and for which the C–H stretch frequency is anharmonically redshifted by 17 cm$^{-1}$. This suggests that the intermediate level $|\sigma^*\rangle$ is formed by the singly excited C–H bend mode.

In the second step, relaxation from this intermediate level occurs. This relaxation from the $|\sigma^*\rangle$ state is exceptionally slow and non-exponential. This suggests that the intermediate state mainly decays to another well-defined state, which slowly decays and acts as a bottleneck for the relaxation. This bottleneck state is probably some low-energy mode of the CHBr$_3$ molecule e.g. the C–Br$_3$ s- or d-stretch modes.

In contrast to solutions of CHBr$_3$ and pure CHCl$_3$, an induced absorption remains around 3022 cm$^{-1}$ after the second relaxation. This absorption persists until at least a delay of 4.7 ns. The cause of this absorption is thought to be the long-living population of the bottleneck state, which frustrates thermalisation.