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### Ultrafast redistribution of vibrational energy in liquids

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**Publication date**  
2002

[Link to publication](#)

#### **Citation for published version (APA):**

van den Broek, M. A. F. H. (2002). *Ultrafast redistribution of vibrational energy in liquids*. [Thesis, externally prepared, Universiteit van Amsterdam].

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## SUMMARY

This thesis is devoted to the investigation of the dynamics of excited vibrations of small molecules and complexes in liquid solution and in the pure liquid. When excited vibrational states decay, energy is transferred to other modes, eventually leading to an equilibration over all degrees of freedom. The lifetime  $T_1$  of the excited state, which is usually on the order of picoseconds in the condensed phase, depends on both the nature and the availability of the accepting modes. By looking at the lifetimes and vibrational dynamics of excited vibrations, a lot of information can be gathered on the couplings that exist within and between molecules.

The lifetimes and vibrational dynamics of several excited molecular vibrations are in this thesis investigated with vibrational pump-probe spectroscopy. In a pump-probe experiment, a pump pulse excites a vibration of a significant fraction of the molecules in a sample. This excitation causes a decrease in the absorbance of the sample, as there are less molecules in the vibrational ground state that can absorb radiation at the  $\nu = 0 \rightarrow \nu = 1$  transition frequency. The transmittance change is measured with a weaker probe pulse that passes through the sample after a variable delay, so that the evolution of the excited vibration can be followed in time. This form of time-resolved spectroscopy requires the light pulses to be shorter than the typical time scale of the decay of the excitation.

The transition frequencies of the molecular vibrations that were studied lie in the mid-infrared, corresponding to wavelengths of 1–10  $\mu\text{m}$ , so short mid-infrared (laser) pulses are needed. There are few lasers that emit in this wavelength region, therefore in most experiments non-linear optical processes like difference-frequency generation (DFG) and optical parametric generation and amplification (OPG/OPA) are used to generate "ultrashort" mid-infrared pulses from the output of lasers that emit in the visible or near-infrared.

Two different hydrogen-bonded acid-base complexes were investigated. A relatively weak hydrogen bond was encountered in complexes of hydrogen chloride (HCl) with diethyl ether  $[(\text{CH}_3\text{CH}_2)_2\text{O}]$ . The lifetime of the excited H–Cl stretch vibration was determined to be  $0.9 \pm 0.2$  ps. The relaxation is found to occur via an intermediate state with the low-frequency  $(\text{CH}_3\text{CH}_2)_2\text{O} \cdots \text{H}-\text{Cl}$  hydrogen bond as the main accepting mode of the vibrational energy. The excited population of this hydrogen-bond mode decays in a second relaxation process with a time constant of  $3.1 \pm 0.5$  ps. In hydrogen-bonded complexes of the acid hydrogen fluoride (HF) with amines, the hydrogen-bonding between the acid HF and the amine base is very strong. We studied the vibrational dynamics of the HF/FHF stretch combination absorption band of complexes of HF with the weak organic base pyridine in diluted pyridine solution. The relaxation of this excited vibration was also observed to occur in two steps. In the first step, energy is transferred from the excited combination vibration to the F–H $\cdots$ F hydrogen bond modes with a time constant of  $0.51 \pm 0.09$  ps. In a second step, with a time constant of  $2.6 \pm 0.3$  ps, energy is transferred from the F–F hydrogen bond modes to lower-frequency modes, leading to a local thermalisation of the energy. Although the hydrogen-bond strengths are very different in both acid-base complexes, in

both cases a similar relaxation mechanism is seen, where the hydrogen-bond mode is the main accepting mode in the first step of the relaxation.

The relaxation of an excited molecular vibration can be an *intramolecular* process, in which energy is transferred to other vibrations in the same molecule, through anharmonic couplings with the vibrational mode that was originally excited, or an *intermolecular* process, in which energy is transferred to vibrations of neighbouring (solvent) molecules or to low-frequency (solvent) modes. Two-colour pump-probe experiments on the C–H stretch vibration of pure bromoform ( $\text{CHBr}_3$ ) show that, compared to solutions of bromoform, the reduction in the number of accepting modes provided by the solvent for intermolecular energy transfer, greatly influences the mechanism and time scale of vibrational relaxation. The relaxation of the excited C–H stretch vibration in pure  $\text{CHBr}_3$  occurs with a time constant of  $43 \pm 1$  ps via an intermediate level, which causes a transient redshift of the C–H stretch frequency. We identified the intermediate level with the singly excited C–H bend mode. We observed that relaxation from this intermediate level is exceptionally slow and non-exponential, which suggests the presence of a “bottleneck” in the relaxation, in contrast to pure chloroform ( $\text{CHCl}_3$ ) and solutions of bromoform. The population of this bottleneck state is very long-lived, which frustrates thermalisation.

The influence of the number of vibrational modes in a molecule on intramolecular vibrational relaxation, is manifested in the investigation of the vibrational dynamics after excitation of the C–O stretch vibration of the alcohols methanol and ethanol in carbon tetrachloride ( $\text{CCl}_4$ ) solution. The relaxation of the excited C–O stretch vibration was observed to occur in two steps. In the first step energy is transferred from the  $\nu = 1$  state of the C–O stretch vibration to an intermediate state with a time constant of  $3.2 \pm 0.2$  ps for methanol and  $3.2 \pm 0.7$  ps for ethanol. The intermediate state is most likely formed by the  $n = 3$  or 4 state of the C–O–H bending mode, which is also known as the torsional mode. In the second step energy is transferred from this intermediate state to low-energy modes, leading to a full equilibration of the energy. In methanol this thermalisation occurs with a time constant of  $28 \pm 1$  ps. In ethanol the second step is faster, with a time constant of  $12 \pm 2$  ps, because of the higher number of available accepting modes.

In the last chapter of this thesis, we focus on the non-linear optical process that is conveniently used to generate the mid-infrared pulses for the experiments featured in the other chapters. The focus is on the correlation properties of parametrically generated light. These properties arise from the fact that OPG is a very special type of conversion process, where one starts with an electromagnetic wave at one frequency and ends up with waves at three frequencies. This process can only be understood using a quantum mechanical description of the electromagnetic field. The parametrically generated light is the macroscopic manifestation of the quantum fluctuations of the zero-photon electromagnetic field that seed the parametric generation process. The temporal coherence or correlation time  $\tau_c$  of parametrically generated mid-infrared light is determined by measuring the twin-correlation peak in the sum-frequency spectrum as a function of delay between the signal and idler. The correlation time  $\tau_c$  of the generated signal and idler fields was found to lie in the picosecond range and is related to the bandwidth  $\Delta\omega$  by  $\tau_c = 1/\Delta\omega$ .