Ultrafast redistribution of vibrational energy in liquids
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I  INTRODUCTION

1.1  BRIEF HISTORY OF OPTICS

The adage “in the country of the blind, the one-eyed man is King” is a good illustration of the great appreciation there has always been for light and the sense of vision. For a long time, sources of light like the sun, fire or lightning were only encountered with religious reverence. The perspective changed when scientific reasoning took hold and systematic observations were made and theories were formulated in the field of optics. The notion that light can be thought of as rays was already conceived in antiquity by Euclides of Alexandria (325 – 265 BC). In his work Optica, he noted that light travels in straight lines and he described the concept of perspective. Euclides followed the Platonic tradition that vision is caused by rays that emanate from the eye. This theory of vision was also propagated a few centuries later by Heron of Alexandria (around 10 – 75) who derived the law of reflection by a geometrical method in his Catoptrica. This work was previously attributed to Claudius Ptolemaeus (85 – 165). Ptolemaeus did author a work devoted to optical phenomena, Optica. The last book of this five-volume edition includes a study on refraction, especially the refraction suffered by light from celestial bodies travelling through air.

The first correct explanation of vision was given by the Arabian scholar Abu Ali al-Hasan ibn al-Hasan ibn al-Haytham (965 – 1040), also known as Alhazen or al-Hazen. He noted that light is the same, irrespective of the source, and that light is reflected from an object into the eye. Al-Haytham formulated his findings and theories on optics after extensive experimental work, where he used spherical and parabolic mirrors and investigated the refraction of light. He also was the first to mention the use of a camera obscura. With his seven-volume work Kitab al-Manazir (translated in Latin as Opticae thesaurus Alhazenī in 1270), he is often considered the father of modern optics.

The field of optics was greatly advanced by the many discoveries from the 17th century onwards, starting when Johannes Kepler (1571 – 1630) discovered the concept of total internal reflection. The discovery and formulation of the law of refraction by Willebrord Snell (1580 – 1626) and the formulation of a wave theory of light by Christiaan Huygens (1629 – 1695) in his book Traité de la lumière,123 are probably the most significant achievements of that era, providing the basis for many discoveries and advances in the centuries to follow. One other name from the 17th century which should be mentioned is of course Isaac Newton (1643 – 1727), who observed the dispersion of sunlight and who, in contrast to Huygens, proposed a corpuscular nature of light in his work Opticks.19

In the centuries to follow many discoveries and theories were put forward by people like Young, Fraunhofer, Brewster, Fresnel, and Faraday, to name but a few. The conclusion that light is an electromagnetic wave and the mathematical formulation by James Clerk Maxwell (1831 – 1871) was another significant step forward in the field of optics and the description of light and its interaction with matter. Another significant advance was however made
by Albert Einstein (1879 – 1955) with the notion that light is quantised. Einstein also proposed that stimulated emission should occur in addition to spontaneous emission and absorption. Elements from the field of quantum mechanics in the first decades of the 20th century strengthened the notion that light is quantised and that it can be viewed both as particles and as electromagnetic waves.

In 1954 an experimental device was described that produced coherent electromagnetic radiation in the microwave-regime. This apparatus was later dubbed maser, an acronym for Microwave Amplification by Stimulated Emission of Radiation. This source of radiation with a very narrowly defined frequency was first greeted with disbelief, as for example Von Neumann was said to have declared: “That can’t be right”. Four years later Townes and Schawlow proposed to extend this principle to optical frequencies, giving rise to the laser, which was an acronym for Light Amplification by Stimulated Emission of Radiation. The first laser was described in 1960, producing coherent visible light from a set-up based on a rod of ruby as the active medium. The high intensities and coherence of the electromagnetic radiation gave rise to a new area of in the field of optics: non-linear optics, of which some aspects are described in the following section. For a comprehensive overview of different types of lasers, that have been developed over the years, see e.g. References 199, 212, and 213.

1.2 Non-linear Optics

The first non-linear optical experiment was the second harmonic generation experiment, reported in 1961 by Franken et al. They passed a red ruby laser beam with a wavelength of 6943 Å through a quartz crystal and observed ultraviolet radiation from the crystal at 3471 Å, which is twice the frequency or half the wavelength of the original laser beam. The dielectric response of a medium is generally described by the dielectric polarisation \( P \), which is a function of the electric field \( E \). Second harmonic generation is one of the processes that can occur when the dielectric response of a medium is no longer predominantly linear in terms of \( E \), meaning that higher-order terms become non-negligible. These higher-order terms only become non-negligible at high field strengths. At optical frequencies, the high intensities corresponding to these high field strengths are only practically attainable with the use of a laser. With the ongoing development of the laser, many experiments were carried out involving optical phenomena connected with the lowest order non-linear term. These phenomena include second-harmonic generation (SHG), sum-frequency generation (SFG), difference-frequency generation (DFG), and optical parametric generation (OPG) and optical parametric amplification (OPA).

These so-called three-wave mixing processes were and still are a useful way to generate coherent radiation at other frequencies than the different types of lasers can provide and many areas of spectroscopy have benefited from these techniques. For example, very few lasers are available that emit in the mid-infrared (wavelengths in the region 1–10 \( \mu m \)), but DFG and OPG/OPA provided coherent and tunable sources for spectroscopy in this wavelength region. The development of pulsed lasers with short pulses was another great achievement which opened up new areas of spectroscopy. With shorter and shorter pulse durations, from nanosecond, through picosecond to the femtosecond titanium-sapphire
lasers of today, peak powers and time-resolutions in experiments have become higher and higher.\textsuperscript{39,103,109,112} Recently, even pulses with sub-femtosecond ("attosecond") duration have been reported.\textsuperscript{1,2} One area of spectroscopy which has greatly benefited from developments in non-linear optics is time-resolved vibrational spectroscopy, which is the experimental technique used in Chapters 3, 4, 5, and 6, and which is introduced in Section 2.2.

In the linear case, the dielectric polarisation $P(r, t)$ at a time $t$, which describes the dielectric response of a medium, can be written as\textsuperscript{90}

$$P(r, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(1)}(r - r_1, t - t_1) \cdot E(r_1, t_1) \, dr_1 \, dt_1,$$  \hspace{1cm} (1.1)

where $\chi^{(1)}$ is the linear susceptibility and $E(r, t)$ the electric field at position $r$ and time $t$. Let $E$ be a monochromatic plane wave with

$$E(r, t) = \tilde{E}(k, \omega) = \int \int E(k, \omega) e^{i(k \cdot r - \omega t)} \, dk \, d\omega,$$  \hspace{1cm} (1.2)

where $k$ is the wave vector, $k = n(\omega) \omega / c$, with $n(\omega)$ the refractive index at frequency $\omega$ and $c$ the velocity of light. The Fourier transform of Equation (1.1) then yields the relation

$$P(r, t) = \tilde{P}(k, \omega) = \chi^{(1)}(k, \omega) \cdot \tilde{E}(k, \omega),$$  \hspace{1cm} (1.3)

with

$$\chi^{(1)}(k, \omega) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(1)}(r, t) e^{-i(k \cdot r - \omega t)} \, dr \, dt.$$  \hspace{1cm} (1.4)

The linear dielectric constant $\varepsilon(k, \omega)$ is related to $\chi^{(1)}(k, \omega)$, in Gaussian units, by

$$\varepsilon(k, \omega) = 1 + 4\pi \chi^{(1)}(k, \omega).$$  \hspace{1cm} (1.5)

In the electric-dipole approximation, when the magnetic dipole and higher-order multipoles can be neglected, $\chi^{(1)}(r, t)$ is independent of $r$ and hence, both $\varepsilon(k, \omega)$ and $\chi^{(1)}(k, \omega)$ are independent of $k$.

In the non-linear case, the polarisation $P$ can be expanded into a power series of $E$:

$$P(r, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(1)}(r - r_1, t - t_1) \cdot E(r_1, t_1) \, dr_1 \, dt_1 + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \chi^{(2)}(r - r_1, t - t_1; r - r_2, t - t_2) \cdot E(r_1, t_1) E(r_2, t_2) \, dr_1 \, dt_1 \, dr_2 \, dt_2 + \cdots$$  \hspace{1cm} (1.6)

where the tensors $\chi^{(n)}$ are the $n^{th}$ order susceptibilities of the medium. If $E$ can be expressed as a group of monochromatic plane waves

$$E(r, t) = \sum_i \tilde{E}(k_i, \omega_i),$$  \hspace{1cm} (1.7)

then the Fourier transform of Equation (1.6) gives

$$P(k, \omega) = \sum_{n \geq 1} \tilde{P}^{(n)}(k, \omega)$$  \hspace{1cm} (1.8)
with

\[ P^{(1)}(k, \omega) = \chi^{(1)}(k, \omega) \cdot E(k, \omega), \]

\[ P^{(2)}(k, \omega) = \chi^{(2)}(k_1 + k_2, \omega_1 + \omega_2) : E(k_1, \omega_1)E(k_2, \omega_2), \]  \hspace{1cm} (1.9)

and

\[ \chi^{(2)}(k_1 + k_2 + \cdots + k_n, \omega_1 + \omega_2 + \cdots + \omega_n) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \chi^{(2)}(r - r_1, t - t_1; \cdots; r - r_n, t - t_n) \times e^{-i(k_1 r_1 + k_2 r_2 + \cdots + k_n r_n)} dr_1 dt_1 \cdots dr_n dt_n. \]  \hspace{1cm} (1.10)

Three-wave mixing processes involve the second order term in this expansion and can therefore only occur in non-centrosymmetric media, which have a \( \chi^{(2)} \) which is non-zero.\(^{10} \) Consider an electrical field \( E \) consisting of two pulses with central frequencies \( \omega_1 \) and \( \omega_2 \)

\[ E(r, t) = E_1(r, t)e^{-i(\omega_1 t - k_1 r)} + E_2(r, t)e^{-i(\omega_2 t - k_2 r)} + \text{c.c.}, \]  \hspace{1cm} (1.11)

where c.c. stands for complex conjugate. When using short laser pulses in three-wave mixing processes at frequencies away from any resonances, the dispersion of \( \chi^{(2)} \) can be neglected and the second-order term in Equation (1.6) can be written as

\[ P^{(2)}(r, t) = \chi^{(2)} : E(r, t)E^*(r, t), \]  \hspace{1cm} (1.12)

indicating an instantaneous dielectric response to the incoming short pulses. Using Equation (1.11), we can write Equation (1.12) as\(^8 \)

\[ P^{(2)}(r, t) = \chi^{(2)}[E_1^2 e^{-i(\omega_1 t - k_1 r)} + E_2^2 e^{-i(\omega_2 t - k_2 r)} + 2E_1E_2^* e^{-i(\omega_1 t + \omega_2 t) - (k_1 + k_2) r} + \text{c.c.}] + 2\chi^{(2)}[E_1^2 + E_2^2]. \]  \hspace{1cm} (1.13)

The terms in this expression correspond to the second harmonic of the field at \( \omega_1 \), the second harmonic of the field at \( \omega_2 \), the sum-frequency generation at frequency \( \omega_1 + \omega_2 \), the difference frequency generation at \( \omega_2 - \omega_1 \) and the optically rectified signal, respectively. For a more comprehensive overview of the subject of three-wave mixing see References 28, 38, 45, 64, 185, 190, 212, and 213.

For the field generated at the sum frequency \( \omega_3 = \omega_1 + \omega_2 \) with wave vector \( k_1 \), the component of the second-order polarisation will have the form

\[ P^{(2)}(r, t)_{\omega_3 = \omega_1 + \omega_2} \propto 2E_1E_2^* e^{-i(\omega_3 t - (k_1 + k_2) r)}. \]  \hspace{1cm} (1.14)

A high intensity at frequency \( \omega_1 \) will only occur if the phase matching condition

\[ k_1 = k_1 + k_2 \]  \hspace{1cm} (1.15)

is satisfied. DFG involves two fields with comparable magnitude, when two relatively intense laser pulses with frequencies \( \omega_1 \) and \( \omega_2 \) (\( \omega_1 \)) are used to generate a third pulse at frequency \( \omega_3 \) (\( \omega_2 \). OPA can be considered a special case of DFG where one of the incident pulses is much lower in intensity than the other. The intense pulse is normally called the pump
pulse. The other two fields are called signal and idler, where generally the idler is the one lowest in frequency. In the remainder of this chapter and in the next chapter, the pump frequency will be denoted by $\omega_1$, the signal frequency by $\omega_2$, and the idler frequency by $\omega_3$.

For collinearly propagating beams the phase matching condition can be written as

$$n_1(\omega_j)\omega_j = n_1(\omega_1)\omega_1 + n_2(\omega_2)\omega_2.$$  \hfill (1.16)

Condition (1.16), in combination with energy conservation $\omega_j = \omega_1 + \omega_2$, can normally only be satisfied in birefringent materials, as in normal materials $n(\omega)$ usually increases monotonically with $\omega$. However, in birefringent materials, the refractive index differs for different directions of the polarisation. Hence, if one of the three linearly polarised waves has a polarisation perpendicular to the others, condition (1.16) can be satisfied. Three different polarisation geometries can be identified: in type I phase matching the pump polarisation is perpendicular to signal and idler; in type II the signal polarisation is perpendicular to pump and idler; and in type III the idler polarisation is perpendicular to pump and signal.

Light polarised perpendicular to the plane containing the propagation vector $\mathbf{k}$ and the optical axis of a uni-axial birefringent material is said to have the ordinary polarisation and experiences a refractive index $n_o$. Light polarised parallel to the plane containing the propagation vector $\mathbf{k}$ and the optical axis of the material is said to have the extraordinary polarisation and experiences a refractive index $n_e$. For extraordinary polarisation, the refractive index will depend on the angle $\theta$ between the direction of propagation and the optical axis, according to the relation

$$\frac{1}{(n^2)^2(\theta)} = \frac{\sin^2 \theta}{(n^2)^2} + \frac{\cos^2 \theta}{(n^e)^2},$$  \hfill (1.17)

where $n^o$ is the principal value for $n^e$ at $\theta = 90^\circ$.

For the case of type I phase matching with collinear propagating beams Equation (1.16) has the form

$$n_1(\omega_1, \theta)\omega_1 = n_1^o(\omega_1)\omega_1 + n_2^e(\omega_2)\omega_2,$$  \hfill (1.18)

where the superscripts $o$ and $e$ stand for ordinary and extraordinary, respectively. Combining Equations (1.17) and (1.18), one can calculate phase-match angles for the type I process for different combinations of $\omega_1$ and $\omega_2$ using the Sellmeier dispersion relations for the refractive indices. It is clear that by rotating the crystal, one can tune the frequencies of signal and idler, as at each angle the phase-matching condition for a different pair of signal and idler frequencies is fulfilled. This method of frequency tuning is generally known as angle tuning. For some crystals, like for example lithium niobate (LiNbO$_3$), the birefringence is also strongly dependent on temperature. This offers the possibility of tuning the frequency of signal and idler by temperature tuning.

### 1.3 Molecular Vibrations and Vibrational Dynamics

The atoms of molecules vibrate around their equilibrium positions. Let us first consider the vibration of the simplest molecule, a diatomic molecule, like hydrogen chloride (HCl) or carbon monoxide (CO). In these diatomic molecules there is one vibrational mode, the
stretch mode, in which the relative distance of the atoms changes periodically with the period of oscillation. To determine the energy levels of this vibration, we first assume that the atoms are driven back by a restoring force, which is proportional to the displacement from the equilibrium distance \( r_e \). The potential \( V(r) \) can be described in terms of a harmonic oscillator with a force constant \( k \) along the line connecting the two atoms and has the form:

\[
V(r) = \frac{k}{2} (r - r_e)^2, \tag{1.19}
\]

where \( r \) is the internuclear distance and \( r_e \) the equilibrium distance. The eigenfrequency of this harmonic oscillator is given by

\[
\omega = \sqrt{\frac{k}{\mu}}, \tag{1.20}
\]

with \( \mu \) the reduced mass of the system. Solving the time-independent Schrödinger equation with the potential of Equation (1.19) leads to the following energy levels

\[
E_n = \hbar \omega \left( \nu + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \ldots \tag{1.21}
\]

In this equation, \( \omega \) is the oscillator frequency, \( \hbar = h/2\pi \), with \( h \) Planck's constant and \( \nu \) the vibrational quantum number. The lowest energy is the zero-point energy \( E_{n=0} = \hbar \omega/2 \). The energy levels associated with this parabolic potential have an equal spacing of \( \hbar \omega \).

In reality, the potential curve of a diatomic molecule is not parabolic. In fact, it is easy to see that the potential must be asymmetric with respect to the equilibrium distance \( r_e \). For distances \( r < r_e \), a reduction of the distance \( r \) will lead to an increase in repulsion, as at short range a repulsive potential is superposed on the parabolic potential, which prevents the two nuclei from penetrating each other. On the other hand, increasing the distance from \( r_e \) will eventually lead to dissociation, as the chemical bond is weakened. So for \( r > r_e \) the potential will become flatter. An often used potential which agrees well with experimental evidence is the so-called Morse potential:

\[
V(r) = E_d \left( 1 - e^{-\zeta(r-r_e)} \right)^2, \tag{1.22}
\]

Here, \( E_d \) is the depth of the potential well and \( \zeta \) is a quantity, characteristic for the molecule under consideration:

\[
\zeta = \omega_h \sqrt{\frac{\mu}{2E_d}}, \tag{1.23}
\]

where \( \omega_h \) is the harmonic oscillator frequency. Solving the Schrödinger equation for the anharmonic oscillator with Equation (1.22) as the potential energy, yields the energy levels, which are given by:

\[
E_n = \hbar \omega_h \left( \nu + \frac{1}{2} \right) - x \hbar \omega_h \left( \nu + \frac{1}{2} \right)^2, \tag{1.24}
\]

where the terms with higher powers of \( \nu + \frac{1}{2} \) have been neglected, as their contributions are very small for small values of \( \nu \). The number of bound levels is finite. The constant \( x \) is the anharmonicity constant, which is defined as

\[
x = \frac{\hbar \omega_h}{4E_d} = \frac{\zeta^2 \hbar}{2\mu \omega_h}, \tag{1.25}
\]
and is usually of order 0.01.

If we rewrite Equation (1.24) in the form

\[ E_v = \hbar \omega_h \left( \nu + \frac{1}{2} \right) \left[ 1 - x \left( \nu + \frac{1}{2} \right) \right], \tag{1.26} \]

and compare with Equation (1.21), we see that going from the harmonic to the anharmonic oscillator, the vibrational frequency \( \omega \) is replaced by

\[ \omega_v = \omega_h \left[ 1 - x \left( \nu + \frac{1}{2} \right) \right] . \tag{1.27} \]

From Equation (1.27) it is clear that with increasing vibrational quantum number \( \nu \), the spacing, i.e. the transition frequency, between the energy levels, decreases, which is illustrated in Figure 1.1. The dissociation energy \( E_o \) is slightly less than the depth \( E_d \) of the potential well containing the bound states, because of the zero-point energy: \( E_o = E_d - \hbar \omega_h/2 \).

The occupation of the energy levels \( E_v \) is in thermal equilibrium proportional to the Boltzmann factor \( e^{-E_v/kT} \). Since at room temperature, \( kT \) corresponds to about 200 cm\(^{-1} \), the stretch vibration of most diatomic molecules will be in the vibrational ground state, for example for HCl molecules, \( E_{\nu=1} - E_{\nu=0} = 2886 \text{ cm}^{-1} \).\(^{178}\)

Molecules with more than two atoms have more vibrational degrees of freedom than a diatomic molecule and therefore have more vibrational modes than the single stretch mode of a diatomic molecule. The vibrations in a polyatomic molecule are often described in terms of normal modes. A normal mode is a synchronous motion of atoms or groups of

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\(^{178}\)In spectroscopy, the unit cm\(^{-1} \) is formally the unit of the quantity \( \bar{v} \), the wave number, the inverse of wavelength. The unit is however also often used for frequency (corresponding to light in vacuum with that wave number) and for energy (the energy of a photon with that wave number).
atoms in a polyatomic molecule that may be excited without leading to the excitation of any other normal mode. The normal-mode coordinates form a basis set for a description of the displacements of the centres of mass of the atoms in a molecule. The number of normal modes in an $n$-atomic molecule is equal to the number of its vibrational degrees of freedom which is $3n - 6$, or $3n - 5$ for a linear molecule. The symmetry of the normal mode is the same as the symmetry of the first vibrationally excited state of the molecule, which provides a way to determine whether a vibrational mode is active, i.e. whether the electric dipole transition associated with the excitation of that mode is allowed.

If the Hamiltonian of a molecule only contains terms of first and second order in the nuclear coordinates, the normal modes are decoupled from each other and can be described as independent harmonic oscillators. In reality, however, the Hamiltonian will also contain third- and higher-order terms. These anharmonicities cause the vibrational potential to more closely resemble a Morse potential than a harmonic potential (diagonal anharmonicity). Additionally, anharmonic couplings exist between the different normal modes in a molecule, giving rise to combined or combination vibrations (cross anharmonicity). For a comprehensive treatment of the vibrations of polyatomic molecules, see e.g. References 11, 12, 97, 108, and 115.

When excited vibrational states decay, energy is transferred from the vibrational mode which was originally excited to other modes, eventually leading to an equilibration over all degrees of freedom. Both the nature and the availability of these accepting modes strongly influence the lifetime $T$ of the excited state. 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. The other type of mechanism is an intermolecular process, in which energy is transferred to vibrations of neighbouring (solvent) molecules or to low-frequency (solvent) modes. When the first step involves intramolecular energy transfer, one of the following steps involves intermolecular energy transfer, as eventually all energy is transferred to the heat bath formed by low-frequency modes, phonons in the case of solids and low-frequency liquid modes in the case of liquids.

If the frequency of the accepting mode is relatively high, which is usually the case with an intramolecular relaxation process, relaxation of an excited vibration is faster, i.e. the lifetime $T$ is shorter (in one step, energy transfer to e.g. two quanta of a molecular vibration is “easier” than to a much larger number of low-frequency modes). If there are no high-energy intramolecular vibrations to which the excited mode can couple, the lifetime will be long and will also be more strongly influenced by the solvent, as the relaxation mechanism will be an intermolecular process. Because the accepting modes are then formed by low-frequency solvent modes, there will also be a strong dependence on temperature. The strong influence of the availability of accepting modes is clearly illustrated in the lifetimes of different C–O stretch vibrations, described in Section 6.1. It is clear that 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 in the condensed phase. For more details on the theory of vibrational dynamics and vibrational relaxation see e.g. References 15, 71, 128, 154, and 202 and references therein.

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2 The energy gap law states that the vibrational relaxation rate is proportional to $\delta^{-N}$, where $N$ is the number of quanta dissipated in the accepting mode and $\delta \ll 1$, with $\delta$ a constant.\textsuperscript{164}
1.4 Absorption Line Broadening of Vibrational Transitions

In the gas phase, the absorption spectrum of a molecular vibration has a characteristic substructure due to the coupling of vibration and rotation of these molecules. In the condensed phases, liquid and solid, the absorption spectrum often shows very broad bands, with very little structure, as is illustrated in Figure 1.2.

The broadening of absorption lines is caused by dephasing: a loss of coherence of the excited oscillators. The broadening can be caused by different mechanisms. There can be a static distribution of transition frequencies of the molecules. The dephasing can also be caused by the loss of coherence due to rapid changes in frequency of the oscillators around one central frequency, without the loss of excitation. And thirdly, decay of the excited state population with a time constant $1/T_i$ also contributes to dephasing.

If the dephasing is due to a static distribution of transition frequencies, which leads to a Gaussian line shape, an absorption line is inhomogeneously broadened. The two other dephasing mechanisms contribute to the homogeneously broadened, characterised by the homogeneous dephasing time $T_2$. The resulting absorption line will have the shape of a Lorentzian with a width $\Delta \nu$ given by

$$\Delta \nu = \frac{1}{\pi T_2}. \quad (1.28)$$

$T_2$ has two contributions:

$$\frac{1}{T_2} = \frac{1}{2T_i} + \frac{1}{T_2^*}, \quad (1.29)$$

where $T_i$ is the lifetime of the excited state and $T_2^*$ is the pure dephasing time. Pure dephasing encompasses all dephasing not due to population relaxation.

In practice, the vibrational absorption bands in the condensed phase at room temperature are inhomogeneously broadened and are composed of an inhomogeneous distribution of homogenously broadened bands. For high-frequency molecular vibrations like the O–H
and C–H stretch vibrations, the homogeneous linewidths are mainly determined by pure dephasing, due to rapid fluctuations and only have a small contribution due to population relaxation. Measuring the linear absorption spectrum will therefore only give information on the width of the distribution of oscillator frequencies and not on the excited-state population relaxation. With non-linear spectroscopical techniques it is however possible to determine $T_\text{r}$ and $T_\text{i}$. The homogeneous dephasing time $T_\text{r}$ can be determined by photon-echo spectroscopy and spectral hole burning. When using these techniques it is usually assumed that the rapid fluctuations, giving rise to the homogeneous broadening, occur on a much faster timescale than the dynamics of the distribution of transition frequencies giving rise to the inhomogeneous linewidth, which are assumed to be very slow on the timescale of the experiment. It is however also possible that the distribution of transition frequencies homogenises during the measurement, a process that is referred to as spectral diffusion. In this thesis, in Chapters 3, 4, 5, and 6, the vibrational lifetime $T_\text{i}$ of several vibrations is determined with vibrational pump-probe spectroscopy, which is introduced in Section 2.2.

1.5 OUTLINE OF THIS THESIS

The largest part of this thesis is devoted to the investigation of the vibrational dynamics of small molecules and complexes in liquid solution and in the pure liquid. The experimental technique that was used is vibrational pump-probe spectroscopy. This form of time-resolved mid-infrared spectroscopy is described in detail in Chapter 2, together with the method of generation of short mid-infrared pulses. In Chapters 3 and 4, the focus is on hydrogen-bonded acid-base complexes in solution. In Chapter 3, a relatively weak form of hydrogen-bonding in complexes of hydrogen chloride with diethyl ether is encountered, whereas in Chapter 4, complexes in which hydrogen-bonding is exceptionally strong come under scrutiny, when complexes of hydrogen fluoride with pyridine are investigated.

The large influence of the nature and availability of accepting modes can be seen in Chapters 5 and 6. In Chapter 5, two-colour pump-probe experiments on the C–H stretch vibration of pure bromoform 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 influence of the number of vibrational modes in a molecule on intramolecular vibrational relaxation, is manifested in Chapter 6. There, the vibrational dynamics are investigated after excitation of the C–O stretch vibration of the alcohols methanol and ethanol in solution.

In Chapter 7, 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 correlation properties of the parametrically generated light reflect the macroscopic manifestation of the quantum fluctuations of the zero-photon electromagnetic field that seed the parametric generation process.