STUDY OF ELECTRON AND ENERGY TRANSFER MODULATION IN MOLECULES USING TIME-RESOLVED VIBRATIONAL SPECTROSCOPY

AN ABSTRACT
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DOCTOR OF PHILOSOPHY
BY

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Abstract

Electron transfer is one of the fundamental processes occurring in many chemical reactions. Electron transfer process has been under intensive study for many applications, for example artificial photosynthesis, where electrons from photo-excited chromophore molecules are harnessed to produce solar fuels in various forms. Transition metal complexes, such as ruthenium and rhenium complexes, play an important role in the continuing development of artificial photosynthetic devices. The electron transfer process in chromophores involving transition metal complexes often occurs on an ultrafast time scale from sub-ps to ns. To resolve such dynamics, ultrafast spectroscopic techniques are required. A variety of ultrafast techniques, such as time-resolved infrared spectroscopy and multi-pulse transient absorption spectroscopy, were used in this study to unravel the excited state electron transfer dynamics in a series of Re(I) complexes.

Transition metal complexes often feature excited states that involve only partial electron transfer between the electron donating and accepting ligands, even for ligands with strong electron donating and accepting properties. It is often difficult to design a compact complex feature a full electron transfer excited state. Therefore, part of the work presented in this thesis was dedicated to the study of the electron transfer extent in the excited states of a series of [Re(N,N)(CO)\textsubscript{3}L]\textsuperscript{+} compounds, where N,N stands for electron accepting and L stands for electron donating ligands. By carefully designing the structure and redox properties of both the electron donor and acceptor, we demonstrated that essentially a full-
electron charge transfer excited state can be prepared, while the designed Re(I) complex is still compact.

To further extend the understanding of the electron transfer in transition metal complexes, modulation of the electron transfer rate in a compact Re(I) complex was studied. By perturbing the electron transfer process with a femtosecond mid-IR pulse, we showed that a 28% increase of the electron transfer rate was achieved. This study demonstrated the possibility of using a small energy mid-IR quanta to change the energy conversion process in a chromophore.

Vibrational energy transfer in molecules is another important process in nature. Detailed understanding of the vibrational energy transfer on a molecule level is fundamentally important and essential for the development of molecular optical devices. It was recently discovered that the transport of vibrational energy in molecules can be fast and efficient due to its ballistic character. To understand the mechanism of the ballistic energy transport, experiments with several series of oligomers were performed using a relaxation-assisted two-dimensional infrared method. The energy transport speed was found to be dependent on transport initiation method and the transport pathways for different cases of initiation were identified. Detailed analysis on the chain band structure, group velocity and vibrational relaxation dynamics is presented.
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During the past years, I have been trying to discover myself as to what a person I want to become after my graduation. This has been a hard question for me to answer, but thanks to the five years I spent in Tulane University, the answer is clearer than ever. Getting a Ph.D. degree is a goal I have been pursuing since I first started my undergraduate studies, and it is a great honor for me to get it from Tulane University. I could not be at where I am now without the help of many people along the way.

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Chapter 1. Introduction

World demand for energy is projected to double every few decades. Incremental improvements in existing energy networks will not be adequate to supply this demand in a sustainable way. Finding sufficient supplies of clean energy for the future is one of the society’s most pressing challenges. The most abundant and fundamental energy source, which has predominantly fueled nature, is sun. More energy from sunlight strikes the Earth in one hour ($4.3 \times 10^{20}$ J) than all the energy consumed on the planet in a year ($4.1 \times 10^{20}$ J). Solar energy has the potential to provide necessary energy with low environmental impact that can be made available to areas with little or no energy infrastructure. The solution of the major challenge in converting sunlight to electricity via photovoltaic solar cells would dramatically reduce the cost/watt of delivered solar electricity, but a factor of ca. 20 is still needed to compete with the primary fossil energy. All routes of utilizing solar energy exploit the functional steps of capture, conversion, and storage. In solar cells, the energy from the sunlight must be captured as excited electron hole pairs in a semiconductor, a dye, or a chromophore. These excited electrons and holes can be tapped off for immediate conversion to electrical power. Of the central importance is the understanding of the electron transfer process in these solar cell devices.
1.1. Electron Transfer

The electron transfer (ET) process is one of the most fundamental and important processes that has been extensively studied over the past 70 years. The development of this field, experimentally and theoretically, represents an intriguing history of human understanding on how nature is functioning through a wide range of chemical and biological processes. In the chemistry world, ET is not only a fundamental process, since it is deeply involved with chemical reactivity, but it also has vast technological implication for areas such as energy conversion (solar cells and batteries) and information storage. More importantly, it is also a linker bringing down the barrier between different sub-branches of chemistry, and encouraging interdisciplinary researches. ET is also a key step in many biological processes, such as photosynthesis and respiration. In the photosynthetic process, the sun light or photons are absorbed to generate electron and holes, which then undergo many well regulated ET processes to create proton gradients, and eventually generate carbohydrate molecules as a form of energy storage. Furthermore, applications in solid state electronics, controlling ET in semiconductors, and molecular electronics, controlling ET between molecules, all require understanding of this fundamental process.

One type of the early experiments in the electron transfer field was on the isotopic exchange reactions, also known as self-exchange reactions (Equation 1.1). In order to explain the ET rate dependence on the solvent and ions size, observed in this type of reaction, Bill Libby adopted the Fanck-Condon principle in his paper in 1952, and introduced the concept of solvent relaxation. In Libby’s treatment, when an electron is
transferred from one molecule to another, both new molecules are formed in the wrong environment of solvent molecules, which imposes a solvation energy barrier to the process. Inspired by the treatment of Libby, which turns out to be incomplete, Marcus realized that for electron transfer occurring in the dark, the energy was not conserved since the products would be formed in a high-energy environment, and only by the absorption of light ("vertical transition") can this process happen. To clarify this problem, Marcus pointed out that fluctuations of various nuclear coordinates of the reactants prior to the electron transfer were needed.\textsuperscript{2-6} With Marcus theory formulated in 1956, Rudolph A. Marcus was recognized by the Nobel Prize for chemistry in 1992. Usually, Marcus theory was used to address systems with outer sphere electron transfer, where the electronic coupling between electron donor and acceptor is weak (non-adiabatic system). For electron transfer reactions, where strong interaction between oxidant and reductant is presented, as often seen in transition metal complexes, inner sphere electron transfer mechanism applies.\textsuperscript{7-8} This field was pioneered by Henry Taube, who was awarded Nobel Prize for chemistry in 1983.

Figure 1.1. Energy surface and kinetics parameters for the electron transfer from reactions to the products in Marcus theory.
Marcus theory can be described by using a reaction coordinate based on the potential energy surfaces of the reactants and the products (Figure 1.1). This theory was derived from the semi-classical treatment of electron transfer by Marcus, and later elaborated by Hush and Sutin. The Gibbs energy profiles along the reaction coordinate can be approximated as parabolas, electron transfer happens by crossing from the parabola of the reactant’s potential energy surface to the products potential energy surface. This process can be describe by the equations below:

\[ k_{er} = A \cdot \exp\left[\frac{-\Delta G^*}{k_B T}\right] \]  
\[ \Delta G^* = \frac{\lambda}{4} \left[1 + \frac{\Delta G^0}{\lambda}\right]^2 \]  
\[ A = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi k_B T}} \]  

where the \( \Delta G^* \) is the free energy barrier between the crossing point and the bottom of the reactant free energy parabola. \( \Delta G^0 \) is the standard free energy for the reactions, and \( \lambda \) is the reorganization energy which is composed of the solvational (\( \lambda_0 \)) and vibrational (\( \lambda_i \)) components: \( \lambda = \lambda_0 + \lambda_i \). The reorganization energy is defined as the change in energy if the reactants were to distort to the equilibrium configuration of the products. \( H_{AB} \) is the electronic matrix element describing the electronic coupling between the reactants’ electronic state and the products’. It is a function of the overlap of the reactants’ orbitals. The magnitude of the electronic coupling energy \( H_{AB} \) is used to distinguish between the two regimes of electron transfer reactions, when the \( H_{AB} \) is small, compared to the
reorganization energy, the electron transfer reaction is said to be non-adiabatic, while if the $H_{AB}$ is large, the electron transfer reaction is adiabatic.

One of the most surprising features of the Marcus Theory is the behavior it predicts in the high $\Delta G^0$ region, known as the Marcus Inverted Region. The rate constant of the electron transfer reaction is predicted to decrease with the increase of the exergonicity. The existence of this region was unequivocally proven experimentally in 1980s.\(^9\)

1.2. Electron Transfer Process in Transition Metal Complexes

Transition metals are defined as elements that have valence shell electrons in d orbitals. Due to the existence of partially occupied d orbitals, transition metals generally exhibit variable oxidation states, and spectroscopic, magnetic or structural features, which make them ideal for excited state electron transfer reactions. For the second or third row d\(^{\pi}\) transition metal (like Ru or Os), coordinative stability between the metal and ligand can be achieved in multiple oxidation states, which enables them to be good electron donors or acceptors. When bonded to ligands with low-lying $\pi^*$ acceptor levels, for example polypyridyl ligands, an intramolecular charge transfer excited state is accessible. Subsequent bimolecular charge transfer processes, of these excited states, have been extensively studied for applications in catalytic reactions,\(^{10-12}\) such as water splitting,\(^{13-14}\) carbon dioxide reduction,\(^{15}\) biomolecule sensing,\(^{16}\) and photo sensitization in different types of photovoltaic reactions.\(^{17-19}\)

One group of transition metal complexes of particular interest are rhenium(I) carbonyl-diimine, fac-[Re(N,N)(CO)\(_3\)L]. They are chemically robust, synthetically flexible and photo-physically active.\(^{20}\) Broad structural variations of the N,N ligand and the L
ligand are possible, which allows fine tuning of the excited state properties and also facilitates the incorporation of these chromophores into a range of media\textsuperscript{21-25} or the attachment to surfaces.\textsuperscript{23} The highest set of occupied molecular orbitals of most fac-[Re(N,N)(CO)\textsubscript{3}L] complexes consists of three dπ(Re) orbitals that mix with π* orbitals of CO group, giving rise to the Re→CO π back bonding.\textsuperscript{26-28} Depending on the molecular orbital energy of the N,N ligand and the L ligand, different excited state character can be expected. When the π*(N,N) orbital is the lowest energy unoccupied orbital (LUMO), which is oftentimes true, the lowest energy excited state would have an electron transfer character from the Re atom to the N,N ligand; this excited state is also known as a Metal-to-Ligand Charge Transfer state (MLCT). In the case that the L is an electron rich ligand, orbitals on L can transfer an electron to π*(N,N) orbitals. This process is known as the Ligand to Ligand charge transfer (LLCT). However, in the case that the L ligand is an electron deficient ligand, equilibrium between two MLCT states (Re→N,N and Re→L) is possible. It is necessary to stress that the types of excited states described above are only limiting cases. In reality, excited states with different characters can be, and often are, mixed. The extent of the mixing depends on the properties of the ligands, as well as the medium (solvent), and can change in the excited state. The identification of a pure excited state character is often times hard to achieve. For example, the formation of a LLCT state is found to be mixed with MLCT state in several different studies,\textsuperscript{29-30} and the charge shifts in those states are typically small (less than one electron). Therefore, part of the work presented in this dissertation is dedicated to the study of the charge shift extent in LLCT states in a set of compact rhenium complexes.
The excited state properties of the rhenium(I) carbonyl-diimine complexes primarily exhibit through their lowest energy triplet excited state, due to the rapid vibrational energy relaxation and intersystem crossing, which has a characteristic time of 100 fs. Many rhenium(I) carbonyl-diimine complexes are emissive and featuring relatively long emission lifetimes in solution, due to existence of a lowest energy triplet MLCT state. For the cases where the MLCT state relaxes through nonradiative decay channel, the energy gap law effect may apply. The energy gap law states that the nonradiative decay rate is found to decrease exponentially with increasing of the energy separation between the excited state and the ground state. The energy gap law for transition metal complexes were experimentally demonstrated by Thomas J Meyer’s group, through the study of a series of osmium (II) polypyridyl compounds with systematically varied redox potential, where a clear exponential dependence of the emission energy and the nonradiative decay rate was observed.

The control of the excited state properties of transition metal complexes was often approached through structural modification. Not only the non-radiative decay processes are effected by the structures of the complexes, but also the excited state electron transfer properties can be modulated by having ligands with different redox potentials. Besides structural modifications, optical modulation, especially mid-IR modulation, of electron transfer has also been demonstrated with several attractive advantages over the structural modification, as it is chemically innocent, easy to control, and potentially mode-specific. For systems with uniquely defined group vibrational modes, modulation of electron transfer rates following excitation of particular modes provides fundamental insight into the degree to which these modes are coupled to the electron transfer process.
A study of mid-IR modulation of the electron transfer in Re(I) complex is presented in this dissertation.

To study the excited state dynamics of transition metal complexes, which occurs on a very short time scale ranging from sub-ps to ns, a variety of time resolved spectroscopic techniques were widely implemented, such as time-resolved infrared spectroscopy (TRIR), IR-perturbed TRIR, transient absorption (TA), time resolved resonance Raman spectroscopy (TR³), femtosecond stimulated Raman scattering (FSRS), and two-dimensional infrared spectroscopy (2DIR). Other spectroscopic techniques including, IR absorption, UV-Vis linear absorption and photoluminescence were also used, sometimes to assist and compliment the time resolved studies. In the case of fac-[Re(N,N)(CO)₃L], the TRIR spectra in the CO stretch vibrational absorption region (around 2000 cm⁻¹) reflect the changes in the electronic and oxidation states of the Re atom, owing to their high sensitivity to the changes of the Re→CO π back bonding orbitals.²¹,²⁸-²⁹ Interactions between multiple CO ligands split the vibrational bands, which typically results in two different combinations of vibrational modes, which is the symmetric CO stretching modes and asymmetrical CO stretching modes. Careful examination of the spectroscopic features of these CO modes, for example the splitting between the two asymmetric CO stretching modes, can also provide information on the excited state molecular geometry; in this case, a more symmetric excited state geometry would result in less splitting. The use of TRIR in photoinduced electron transfer is not limited to spectroscopic feature of the IR active groups, this method can also provide kinetic information of the electron transfer reactions, for example the vibrational energy relaxation and the reorganization of the solvent molecules on the ultrafast time scale.
1.3. Vibrational Energy Transfer through Oligomeric Chain

Besides electron transfer, energy transfer in molecules also plays an essential role in life science, molecular electronics, and development of new materials. Essentially all chemical reactions involve vibrational energy transfer, and for many reactions the vibrational energy flow into reactants and/or out of products plays an essential role. Detailed knowledge of the energy transport properties can lead to optimization of reaction rates and to finding ways of controlling such reactions. Novel technological developments, involving molecular junctions and single molecule electronic devices, require fast energy transport for efficient performance. Two mechanisms, ballistic and diffusive, describe the limiting regimes of the vibrational energy transport. Diffusive energy transport involves Brownian-like energy exchange steps and was observed in numerous molecular compounds including peptides, helices and small molecules. Ballistic energy transport involves free propagation of the vibrational wavepacket and can be very fast and efficient. It requires vibrational states delocalized over the region of transport, thus it benefits from having an ordered oligomeric molecular structure. Fast energy transport with a speed of 9.5 Å/ps along alkane chains self-assembled into a monolayer on a gold surface, initiated by a flash heating of the gold surface, was found by Dlott and coworkers. Ballistic energy transport was also reported in bridged azulene-anthracene compounds initiated by relaxation of an excited electronic state, in single-wall carbon nanotubes, and a few other systems. Ballistic energy transport initiated by a heat gradient, which is typically rather small, occurs via low-frequency acoustic vibrational bands capable of transporting small quanta of energy at a time. With the development of molecular optical devices, much larger excess energy per molecule can be generated, easily
on the level of several thousand wavenumbers. Understanding the pathways of efficient
dissipation of such energy, and the ways of delivering large quanta of energy to a target for
further use, is important for the optimization and development of these optical devices. The
ability of optical phonon bands to efficiently transfer energy has been predicted by Nitzan
and coworkers.\textsuperscript{38, 43} Part of the work in this dissertation (Chapter 7) suggests the realization
of this prediction identifying the specific chain bands responsible for the through-chain
ballistic transport.

1.4. Dissertation Outline

In Chapter 2, the theoretical background of the ultrafast spectroscopic techniques
are demonstrated. The 3\textsuperscript{rd} order signal response and phase matching geometry for 2DIR
experiment are discussed. The detailed description of 3 major spectroscopic setups
including a 3-pulse transient spectroscopy setup, an IR-perturbed TRIR spectroscopy setup,
and a fully automated 2DIR setup, are presented in Chapter 3.

The research target of the first project is to modulate the intramolecular electron
transfer process. This project started with a search for a full electron transfer excited state
in a series of Re metal complexes. Due to the highly mixed nature of the excited states in
the Re complexes, we concluded that a full electron transfer excited state is possible with
one of the complex, where the electron donor is mostly decoupled from the rest of the
molecule, if we lower down its charge transfer state energy even more by using more polar
solvent or structure alternation (Chapter 4). Based on this conclusion, new Re complexes
designed with lower charge transfer state energy were tested with TRIR, DFT calculation,
and many other techniques. We are able to identify a full electron ligand to ligand charge
transfer state in this compact Re complex (Chapter 5). To modulate this full electron
transfer process, a 3-pulse UV pump/mid-IR pump/mid-IR probe method is used. Even though several factors affected the modulation data recorded in this study, a sizable (28%) increase in the electron transfer rate was observed with the present of mid-IR pump pulses (Chapter 6).

In Chapter 7, a study on ballistic energy transfer in a series of oligomeric chains is presented. This study unveiled an interesting and somewhat counter-intuitive nature of the energy transfer process in oligomers. This vibrational energy transfer process has been proved to be ballistic and the energy transfer speed from one end to the other end was dramatically different from the reverse transfer speed. A detailed chain band structure calculation and mode coupling evaluation were used to identify the energy transfer pathways in each case. Group velocity calculations, based on the calculated chain bands, provided a consisted picture with the experimental results.
Chapter 2. Theoretical Background of Nonlinear Spectroscopy

2.1. Introduction

Interactions of laser fields with matter provide powerful tools to understand matter and its dynamics. The ability to control the spatial, as well as the temporal shape of the laser pulses enables new spectroscopic techniques and opens up exciting possibilities. The structure and dynamic process of the matter can be directly probed by its interactions with the laser field. By utilizing light, or in a more general form, electromagnetic radiation, with different frequencies, many valuable tools has been invented, such as nuclear magnetic resonance, infrared, ultraviolet and X-ray spectroscopies.

Of particular interest to this dissertation is infrared spectroscopy. Infrared radiation refers to a part of the electromagnetic spectrum between the visible and microwave regions. Infrared spectroscopy utilizes the interaction between mid-IR radiation and the vibrational motion of atoms in a molecule to interrogate structural information of the molecule. There are generally two types of molecular vibrations: stretching and bending. In a stretching vibration, the distance between moving atoms is increasing or decreasing. However, a bending vibration may contain changes in bond angles between different atoms of groups without the change of inter-atom or inter-group distance as seen in twisting, rocking, scissoring, and wagging vibrations. Only those vibrations that induce dipole moment changes of the molecule are observed in the IR absorption spectrum. With the development of ultrafast laser technology, two-dimensional infrared (2DIR) spectroscopy was invented to extend the application of infrared spectroscopy to the study of not only the absorption of IR active vibrations, but also interaction between different vibrational modes. The coupling between two vibrational modes can provide valuable information on their
structural characters, such as the angle between their transition dipole and the distance between them.

Based on the response of the matter with respect to the applied field, optical techniques can be classified into two categories: linear and nonlinear spectroscopies. Different from IR absorption, where the signal of the measurement scales linearly with the applied field, 2DIR is a nonlinear spectroscopy method, where the 3rd order molecular response is measured. In this chapter, different light-matter interactions, as well as the bases for nonlinear spectroscopy techniques are introduced.

2.2. Nonlinear Spectroscopy

Optical measurements can be classified according to their power-law dependence on the external electric field. The optical polarization $P$ can be defined as:

$$P = P^{(1)} + P_{nl}$$  \hspace{1cm} (2.1)

$$P_{nl} = P^{(2)} + P^{(3)} + \cdots$$  \hspace{1cm} (2.2)

$P^{(1)}$ is the linear polarization that is responsible for the linear optical response, for example light absorption, reflection, and refraction. $P_{nl}$ is the nonlinear polarization, which can be represented by the sum polarization components to the nth power. The nonlinear techniques that utilize nonlinear polarization response can be treated as multi-wave mixing, where the wave vectors of multiple waves, $\vec{k}_1, \vec{k}_2, \cdots$, can be combined to generate a signal wave $\vec{k}$.

$$\vec{k} = \vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3 \pm \cdots$$  \hspace{1cm} (2.3)

In case of two wave mixing, the sum or the difference between the two waves can be generated, which is known as sum frequency generation ($\vec{k}_s = \vec{k}_1 + \vec{k}_2, \omega_s = \omega_1 + \omega_2$)
and difference frequency generation \((\vec{k}_s = \vec{k}_1 - \vec{k}_2, \omega_s = \omega_1 - \omega_2)\). These two processes are widely used in common light conversion devices, such as optical parametric amplifiers (OPA) and optical parametric oscillators (OPO).

### 2.3. Light-Matter Interaction

Consider the electric field interaction with one vibrational mode in a molecule. The electric field can be approximated as a planar wave:

\[
\vec{E}(t) = \vec{E}'(t) \cos(\vec{k} \cdot \vec{r} - \omega t + \phi),
\]

where \(\vec{k}\) is a wavevector that determines the light propagation direction, \(\omega\) is the frequency, \(\phi\) is the initial phase, and \(\vec{E}'\) is the temporal envelope that contains the polarization of the pulse.

The interaction energy in the dipole approximation is given by the scalar product of the molecular dipole operator \(\hat{\mu}\) and the electric field \(\vec{E}\),

\[
\hat{W}(t) = -\hat{\mu} \vec{E}(t)
\]

where the light-molecule interaction is treated semi-classically by considering the time dependent electric field classically, and the vibrational states of the molecule are treated quantum mechanically. The total Hamiltonian \((\hat{H})\) for this system is

\[
\hat{H} = \hat{H}_0 + \hat{W}(t).
\]

where \(\hat{H}_0\) is the Hamiltonian for the unperturbed molecule having eigenfunctions \(|n\rangle\):

\[
\hat{H}_0|n\rangle = E_n|n\rangle.
\]
The time dependence of a wavefunction $|\Psi\rangle$ is governed by the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle.$$  \hspace{1cm} (2.8)

A stationary wave function of the full Hamiltonian can be expressed in the complete basis set $\{|n\rangle\}$, formed by the eigen functions of $\hat{H}_0$:

$$|\Psi\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle,$$  \hspace{1cm} (2.9)

where $c_n$ is a coefficient for each eigenstate $|n\rangle$. With the time-dependent perturbation, $\hat{\mathcal{W}}(t)$, occurring when electric field interacts with the molecule, the coefficients $c_n$ become time dependent. The time dependent $c_n(t)$ coefficients can be determined by substituting Eq. 2.9 into Eq. 2.8.

For a two level system, if one consider the molecule in its ground state $|0\rangle$, transitions to the first excited state $|1\rangle$ due to $\hat{\mathcal{W}}$. The molecule will be in a super position state represented by a linear combination of the eigenstates $|0\rangle$ and $|1\rangle$

$$|\Psi(t)\rangle = c_0 e^{-iE_0 t/\hbar} |0\rangle + i c_1 e^{-iE_1 t/\hbar} |1\rangle.$$  \hspace{1cm} (2.10)

The interaction between the molecule and the electric field can be measured as a macroscopic polarization $P(t)$, which then evolves according to the molecular response (wavefunction) in Eq 2.10. This macroscopic polarization can be measured by detecting the emission field. It can also be calculated as the expectation value of the dipole operator

$$P(t) = \langle \mu \rangle = \langle \Psi(t) |\hat{\mu}|\Psi(t)\rangle.$$  \hspace{1cm} (2.11)
After substituting $|\Psi(t)\rangle$ with Eq. 2.10 into Eq. 2.11, and simplification, $P(t)$ can be approximated as:

$$P(t) \propto +\mu_{01}^2 \sin(\omega_{01} t).$$

(2.12)

where the $\mu_{01}$ is the transition dipoles between $|0\rangle$ and $|1\rangle$, $\omega_{01}$ is the difference frequency between $|0\rangle$ and $|1\rangle$. According to the Maxwell’s equations, oscillating charges creates an electromagnetic wave that is 90˚ phase shifted with respect to the macroscopic polarization. Therefore, the measurable emitted electric field from the molecule is proportional to $-\mu_{01}^2 \cos(\omega_{01} t)$. If we measure this emitted field and then calculate its Fourier transform, we get the absorption spectrum of the molecule. This is also referred to as linear response of the molecule to the electric field.

2.4. Density Matrix and Rotating Wave Approximation

The above consideration derives the response of a single molecule interacting with the electric field. In reality, signals that can be measured are often come from an ensemble of molecules. The derivation of the response function for this case requires the use of a density matrix, where the coefficients of the wavefunctions of individual molecules can be statistically averaged to describe the quantum mechanical coherences and dephasing. Detailed description of density matrix formalism can be found in the reference,\textsuperscript{62-63} here only the basic properties of the density matrix will be introduced.

For a two level vibrational system with quantum states $|0\rangle$ and $|1\rangle$, the density matrix is:

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix}$$

(2.13)
There are two different types of elements in the density matrix, the diagonal elements and the off-diagonal elements. The diagonal elements, \( \rho_{00} \) and \( \rho_{11} \), represent the populations of the corresponding state, while the off-diagonal elements, \( \rho_{01} \) and \( \rho_{10} \), are the quantum mechanical coherences and the source of emitted electric field. With the use of density matrix, the total response function can be obtained:\(^6\)

\[
R^{(1)}(t_1) \propto \sin(\omega_0 t_1) \tag{2.14}
\]

This is the same result as Eq. 2.12, in the limit when the response function equals the polarization.

In the Eq. 2.12 and Eq. 2.14, the response dependence on the electric field \( E(t) \) of the laser pulse has been ignored. A more precise way to represent \( P(t) \) with \( E(t) \) taken into consideration is to solve the time dependent Schrödinger equation include \( E(t) \), which is difficult for an ensemble of molecules. Therefore, linear response theory can be used in this case, assuming the laser pulse is weak and macroscopic polarization scales linearly with the electric field strength. The laser pulse can then be treated as a sum of \( \delta \)-functions that together give the pulse envelope \( E'(t) \). The macroscopic polarization can be represented by convoluting the total response function with the laser pulse:

\[
P^{(1)}(t) = \int_{0}^{\infty} dt_1 E'(t - t_1) R^{(1)}(t_1). \tag{2.15}
\]

The electric field can be expressed as:

\[
E'(t - t_1) \cos(\omega t) = E'(t - t_1) \left( e^{-i\omega(t-t_1)} + e^{+i\omega(t-t_1)} \right) = E(t - t_1) + E^*(t - t_1) \tag{2.16}
\]

where \( E'(t - t_1) \) is the time domain pulse envelope. Substitute Eq. 2.16 into Eq. 2.15:
\[ P^{(1)}(t) = \int_0^\infty dt_1 (E(t - t_1) + E^*(t - t_1)) R^{(1)}(t_1). \]  

(2.17)
after expanding Eq. 2.17, and applying a rotating wave approximation, where the nonresonant term in the equation was neglected, the one term linear polarization can be obtained:

\[ P^{(1)}(t) = \int_0^\infty dt_1 E(t - t_1) R^{(1)}(t_1) \]  

(2.18)

2.5. Nonlinear Response Function

The method, outlined above for derivation of the linear polarization response can be extended to nonlinear responses in a straightforward manner.\textsuperscript{64} For 3\textsuperscript{rd} order interactions, which are relevant for 2DIR experiments, the macroscopic polarization is given as:

\[ P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E_3(t - t_3) E_2(t - t_3 - t_2) \]

\[ \cdot E_1(t - t_3 - t_2 - t_1) R^{(3)}(t_1 t_2 t_3) \]  

(2.19)

with the 3\textsuperscript{rd} order response function

\[ R^{(3)}(t_3, t_2, t_1) = -\frac{i}{\hbar^3} \langle \hat{\mu}(t_3 + t_2 + t_1) \left[ \mu(t_2 + t_1), \left[ \mu(t_1), \mu(0), \rho(-\infty) \right] \right] \rangle \]

\[ \propto i \langle \mu_3 [\mu_2, [\mu_1 [\mu_0, \rho]]] \rangle \]  

(2.20)

2.6. Selecting Phase Matching Pathways

For the 3\textsuperscript{rd} order interaction, the response is described by eq. 2.19, where the \( E_1, E_2 \) and \( E_3 \) are electric field of the three laser pulses. As defined in eq. 2.16, the electric field can contribute to the response by either \( E(t) \propto e^{-i\omega t} \) or \( E^*(t) \propto e^{+i\omega t} \).
Therefore different combinations of electric field are possible, and those combinations, also referred to as pathways, can be described by Feynman diagrams. By carefully designing the experiment, some pathways can be discriminated against the others. One of the common experimental approaches to achieve the discrimination is to take into account phase matching, because each pathway (diagram) depends on different properties of the system.

As described in eq. 2.4, the electric field of laser pulses are not only described by the frequency $e^{\mp i\omega t}$, but also by the initial phase and wavevector via $E(t) \propto e^{-i\omega t + i\phi + ik \cdot \vec{r}}$ or $E^*(t) \propto e^{+i\omega t - i\phi - ik \cdot \vec{r}}$. Therefore, for a single pathway involving $(E^*, E, E)$, the response function can be written in the following way:

$$P_1^{(3)}(t) \propto e^{i(\vec{k}_1 + \vec{k}_2 + \vec{k}_3) \cdot \vec{r}} e^{i(\phi_1 + \phi_2 + \phi_3)} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E'_3(t - t_3)$$

$$\cdot E'_2(t - t_3 - t_2) \cdot E'_1(t - t_3 - t_2 - t_1)R^{(3)}(t_{123})$$

(2.21)

where $E'_n$ represents the envelope and the time dependence of the electric field. The pre-factor keep selecting the pathway as it determines the direction of the emitted field. For example, by placing a detector in the direction of $-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$, one can record 3$^{rd}$ order contribution described by $P_1^{(3)}(t)$. This particular geometry is also known as the rephrasing pathway. The directions of the diagonal and off diagonal signals described by this pathway are shown in Figure 2.1.
Figure 2.1. 2DIR pulse geometry at the sample cell position, $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. A. Pulse geometry and spot pattern for the off-diagonal signal. B. Pulse geometry and spot pattern for the diagonal signal.

Since the photon echo direction is dependent on the directions of all three beams, the spot pattern is different for different frequency combinations (Figure 2.1). In the diagonal geometry, all three laser pulse have the same frequency (energy), therefore the resulting photon echo propagates towards the corner of a square with respect to the other three pulses (Figure 2.1 B). When $\mathbf{k}_1$ and $\mathbf{k}_2$ have the same frequency that is different from that of $\mathbf{k}_3$, the shape of the spot pattern is a trapezium, with the photon echo pointing towards one of its corner (Figure 2.1 A); a cross peak will be measured in the $k_s$ direction.
Chapter 3. Experimental Details

The fully automated 2DIR spectrometer presented in this chapter was described in details in the following paper:


3.1. Introduction

The study of structures and properties of chemical species and their reactions are of center importance to the development of many fundamental field, like chemistry, physics and biology. In all chemical reactions, reactants undergo structural or energy level changes before converts into products. Being able to track the structural changes, as well as the energy flow during the reaction will greatly facilitate the understanding of the reaction mechanism. In biology, the knowledge on the three dimensional structure of biological molecules can result in understanding the mechanism of functioning of those vital species. For example, the detailed mechanism of photosynthesis has been a long-time intriguing puzzle that researchers are still trying to solve. Only very recently, the three dimensional structure of the active site of photosystem(II), which is an oxo-bridged Mn4Ca cluster arranged in a Mn3CaO4 cuboidal framework, has been resolved and led to a more detailed understanding of the electron transfer process in the reaction center. The study of protein structure is also important to understanding protein folding and unfolding, protein-DNA interactions, to name a few. At the same time, the energy transfer process
in molecules has received considerable interest because it is essential for molecular electronics,\(^{71-73}\) and biological system such as micelles.\(^{74-75}\)

A variety of spectroscopic techniques have been developed to study the structure of molecules and materials. 1). Nuclear magnetic resonance (NMR) spectroscopy is a powerful spectroscopic method in both solution phase and solid phase. It has a wide range of applications in studying the dynamics of polymer chains,\(^{76}\) enzyme catalysis,\(^{77}\) and RNA conformational transition.\(^{78}\) NMR utilizes the magnetic radiation in the radio frequency to probe the frequencies of nuclei spin transitions, which depend on the atom type and its chemical environment. Variations of the NMR technique have been developed, for example, the nuclear Overhauser effect NMR spectroscopy (NOESY) and correlation NMR spectroscopy (COSY). However, due to nature of the nuclear spin relaxation time, which is on the order of millisecond or longer, structural changes that occurs faster than the relaxation time cannot be resolved.\(^{79}\) 2). X-ray diffraction (XRD) has been used to map the structure of molecules for a long time. It measures the angles and intensity of the diffracted x-ray beams to determine the three dimensional picture of the density of electrons within the crystal. One of the recent developments for X-ray spectroscopy is the laser-induced time-resolved soft X-ray absorption spectroscopy, which can be used to study structure rearrangement and charge transfer induced by laser excitation.\(^{80-83}\) However, the X-ray diffraction methods are most suitable to analyze samples of crystalline solid, which limits its application.

Optical spectroscopy, in particular, infrared spectroscopy, is a powerful analytical tool for studying molecular structures as well as their changes. The IR spectrum can be divided into three regions: near-IR \((14300 – 4000 \text{ cm}^{-1})\), mid-IR \((4000 – 400 \text{ cm}^{-1})\), and
far-IR (400 – 10 cm⁻¹). Each spectral region can be used to study different energy states of molecules. Mid-IR spectral region corresponds to the vibrational energy levels of molecules; absorption of the mid-IR radiation would drive displacements of the atoms. Therefore the vibrational frequencies are directly linked to the bond strength and mass of the involved atoms. With the development of femtosecond lasers, IR spectroscopic techniques have reached an unprecedented power. Femtosecond lasers, with the ability of generating laser pulses with pulse width well below 100 fs, provide pulses with highly concentrated energy, thus enabling many nonlinear processes only efficient with intense laser field. One of the most powerful techniques made possible by the femtosecond laser is two-dimensional infrared vibrational echo spectroscopy (2DIR), pioneered by Hochstrasser and colleagues. 2DIR probes the vibrational correlation between different vibration modes, which opens new venue for mapping the 3D structures of complicated molecules, and for studying dynamics of their structural changes.

This chapter overviews the instrumentations used in this dissertation. Light conversion techniques using optical parametric amplifier (OPA), and difference frequency generation (DFG) setups are reviewed. Three in-house built setups are described: a femtosecond 3-pulse transient spectroscopy setup, a dual-frequency 2DIR setup, and a fully automated 2DIR instrument.

3.2. Femtosecond Laser Oscillator and Regenerative Amplifier

The first laser was built in 1960 by T. Maiman, to which he coined the name “laser”, as an abbreviation of Light Amplification by Stimulated Emission of Radiation. A year later, the Q-switching technique was invented, enabling the concentrating of laser output into a single short pulse. Q-switching is an important laser technique that is widely used in
many modern laser designs. Shown in Figure 3.1 is a block scheme of the femtosecond laser currently in use in Dr. Rubstov’s lab for the dual-frequency 2DIR experiments.

![Figure 3.1. Block scheme of the femtosecond laser currently in use in Dr. Rubtsov’s lab](image)

The femtosecond oscillator (Vitesse, Coherent) pumped by a frequency-double diode-pumped Nd:YVO₄ laser (Verdi, Coherent) generated femtosecond laser pulses (800 nm) with a pulse width of 44fs, $4 \times 10^{-6}$ mJ energy at 80 MHz repetition rate. The output of the laser oscillator was split into two parts (not shown), one portion of it was sent to an optical-pumped regenerative amplifier (Legend, Coherent) where the pulse energy was amplified by ca. $10^5$ fold to 0.7 mJ energy at the 1 kHz repetition rate. This output was used for a 2DIR setup. The other portion of the laser oscillator output was directed into another regenerative amplifier (Spitfire Pro, Spectra-Physics) to generate pulses featuring 44 fs pulse duration and 1.1 mJ energy at 1 kHz repetition rate. This output was used for a 3-pulse transient spectroscopy setup.
3.3. Generation of Tunable Mid-IR Pulses

3.3.1. Optical Parametric Amplification

The laser pulses generated from the femtosecond laser oscillator and amplifier was centered at ca. 800 nm, and had a relative low frequency tunability. However, for spectroscopic measurements it is essential to have tunable pulses that can cover the spectral region of interest. Therefore, a nonlinear process, known as optical parametric amplification, was exploited to generate laser pulses with tunable frequencies.

Figure 3.2 shows the layout of three in-house built optical parametric amplifiers (OPAs):
Figure 3.2. Layout of three in-house built optical parametric amplifiers. The elements used in this setup are listed in Table 3.1.

Table 3.1. List of optical components used in the in-house built OPAs.

<table>
<thead>
<tr>
<th>Items number</th>
<th>Optical components</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2 – M23</td>
<td>Mirrors</td>
</tr>
<tr>
<td>L1 – L11</td>
<td>Lens</td>
</tr>
<tr>
<td>A1 – A7</td>
<td>Apertures</td>
</tr>
<tr>
<td>NL1 – NL 3</td>
<td>Negative Lens</td>
</tr>
<tr>
<td>BS0 – BS20</td>
<td>Beam splitters</td>
</tr>
<tr>
<td>WP</td>
<td>Wave plate</td>
</tr>
<tr>
<td>LP</td>
<td>Linear Polarizer</td>
</tr>
<tr>
<td>Sapphire</td>
<td>Sapphire crystal</td>
</tr>
<tr>
<td>BBO1 – BBO3</td>
<td>Barium borate crystal</td>
</tr>
<tr>
<td>TS1 – TS6</td>
<td>Translation Stage</td>
</tr>
<tr>
<td>S1 – S6</td>
<td>Spherical Mirrors</td>
</tr>
<tr>
<td>D1 – D3</td>
<td>D-shape Mirror</td>
</tr>
<tr>
<td>PS</td>
<td>Polarization rotating Periscope</td>
</tr>
</tbody>
</table>

The design of the three OPAs is similar, therefore only OPA1 is described, for simplicity, to illustrate its design and operation. The fundamental femtosecond laser output featuring pulses of 44 fs duration and 1.1 mJ energy at 1 kHz repetition rate was split into three portions. The first portion, which only contains a small amount of power, was directed
(reflected by M2 mirror in Figure 3.2) into a white light generation assembly shown on the left side of Figure 3.2. The power of this portion of the fundamental beam was controlled by a wave plate and polarizer pair, before it is focused into a sapphire crystal, where the white light is generated. The generated white light was then collimated and used as a seed beam in the parametric amplification process. The second portion of the fundamental beam, referred to as 1st stage beam, was reflected off the beam splitter BS0, and directed to propagate collinearly with the white light. Both the white light (seed beam) and the 1st stage beam (pump beam) were focused into a $\beta$-BaB$_2$O$_4$ (BBO) crystal, which is a nonlinear crystal suitable for parametric generation/amplification in the visible to near-IR regions. The photon in the pump beam is converted into a lower-frequency signal photon, which equals to the selected seed beam frequency, and an idler photon, which has a frequency equals to the difference between the pump photon and the signal photon. This parametric process is sensitive to the relative phases of the optical pulses involved, therefore efficient conversion requires phase-matching for the specific frequency of interest.

After the first stage amplification, the idler beam was filtered out with a dichroic mirror BS17, while the signal beam passed through and reflected by M7 for the second stage amplification. The third portion of the fundamental beam, referred to as 2nd stage beam, overlapped with the signal beam at a different place in the BBO crystal for second stage amplification. The overall efficient of this two stage collinear OPA is ca. 20%.

### 3.3.2. Different Frequency Generation

The signal and idler pair generated from the OPA, was focused into a different frequency generation unit, as shown in Figure 3.3. The signal and idler were separated by a beam splitter, so that the temporal difference, as well as the directional mismatch,
between the signal and idler can be compensated individually. Then, signal and idler were recombined and overlapped in 1.5 mm thick AgGaS$_2$ crystal, where the difference between the signal and idler frequencies was generated. Same as the parametric amplification process, the difference frequency generation is also a nonlinear process and its efficiency depends on the phase matching condition. Therefore, for different mid-IR frequencies, the angle between the signal-idler beam and the AgGaS$_2$ crystal need to be optimized.

**Figure 3.3.** Optical scheme of DFG assembly.
3.4. Time-Resolved 3-Pulse Transient Spectroscopy Setup

3.4.1. Setup Schematics

With the OPA and DFG blocks, I designed and built a 3-pulse transient spectroscopy setup, capable of conducting 1) Time resolved infrared spectroscopy (TRIR); 2) Transient UV-Vis absorption spectroscopy (TA); 3) IR-perturbed transient absorption spectroscopy. A functional scheme of the system is shown in Figure 3.4.

![Functional scheme of the 3-pulse transient spectroscopy setup.](image_url)

There were three beams in this system: the UV/Vis pump beam, visible probe beam, and the mid-IR beam, which can be used as a pump or probe. The UV/Vis pump was generated by two different methods. The UV beam had a wavelength of 402 nm, generated as the second harmonic of the laser fundamental wavelength. The Vis pump beam was generated by frequency doubling of the Signal output of an OPA, achieving a tunable range from 550 nm to near-IR. A switch between UV and Vis pump beams is simple as common
translation stage (Paker) was used for both beams. White light continuum served as a visible probe beam, covering a spectrum range from 450 nm to 750 nm was generated by using a sapphire crystal as described in the section 3.3.1 and delayed by a translation stage (NRT150, Thorlabs). The mid-IR beam was generated by a DFG assembly built near the sample cell (Figure 3.5), pumped by the OPA output. The detailed implementation of this three pulse system is shown in Figure 3.5.

Figure 3.5. Detailed design and implementation of the 3-pulse transient spectroscopy setup
3.4.2. Time-Resolved Infrared Spectroscopy (TRIR)

The TRIR spectroscopy measurements were conducted using a UV-pump/mid-IR probe pulse sequence, utilizing two beams from the 3-pulse system (Figure 3.4).21 The UV pump and the mid-IR probe beams were focused into the sample resulting in a spot size of 150 and 100 μm, respectively. The UV pump was chopped at half the laser repetition rate, and the transmitted mid-IR beam was measured with a monochromator (TRIAX-190, HORIBA) and a dual channel MCT detector (MCT-11-1.00, Infrared Associates). Because the mid-IR pulse had a spectral width of 200 cm\(^{-1}\), the monochromator was scanned during the measurements to resolve individual frequencies. A spectral resolution of 2 cm\(^{-1}\) or better was achieved. To avoid influence of sample degradation by the UV excitation, a flow cell (DLC2, Harrick) was used in most of the studies described in this dissertation. The flow cell is composed of a Teflon spacer (150 μm thick) sandwiched by two CaF2 windows, and connected with a micro-annular gear pump (mzr-2942, HNP Mikrosysteme). A sample solution of ca. 2.5 ml circulated within this flow cell assembly during the measurement.

The transient spectra measured by TRIR represent the differences between the vibrational spectra in the excited (with UV pump) and ground (without UV pump) electronic states; the positive peaks in the spectra belong to absorption by vibrational modes of the electronic excited state, while the negative peaks are due to the bleaching of ground state absorption peaks. By varying the delay between the UV pump and mid-IR probe, the relaxation dynamics of the sample following the UV excitation was measured.

3.4.3. Transient Absorption (TA)

TA measurements were performed using the UV-pump/Vis-probe pulse sequence. The UV pump beam was chopped at half the laser repetition rate. After passing through
the sample, the visible probe is dispersed by a monochromator, and detected by a CCD array camera. The spectral resolution of 3 nm or better was achieved.

3.5. Dual-Frequency 2DIR Spectrometer

Two independently tunable mid-IR beams were used for the dual-frequency 2DIR measurements.\textsuperscript{85-86} The functional scheme of the “manual” 2DIR setup is shown in Figure 3.6 (a). Each mid-IR beam was split into two equal parts to provide $k_1$, $k_2$, $k_3$, and local oscillator (LO) beams. The delays between these four beams are controlled by three translation stages equipped with linear nano-motors. Because the signals were measured as interferograms by scanning the delays between the mid-IR pulses, the step error of the translation is required to be smaller than $\lambda_{\text{mid-IR}}/50$, which is ca. 50 nm for the mid-IR wavelengths.

To satisfy this requirement, the motions of all three translation stages were measured accurately using a HeNe beam tracking system, where the HeNe beams were reflected from retroreflectors attached to the back side of the moving stages and formed Michelson interferometers.\textsuperscript{87} The interference pattern generated, was measured with two photodiodes, the distance between which was selected so that the signals from the two photodiodes, when the stage moves, oscillate with a $\pi/2$ phase shift. The positions measured by this tracking system were used instead of the positions reported by the nano-motor controllers.

The polarizations of $k_1$, $k_2$, $k_3$ were controlled by a combination of wave plate and wire-grid polarizer, which allows the setting of any polarization for each beam. These three beams were then focused onto the sample with a 51 mm focal length, gold coated, off-axis
parabolic reflector. The photon echo signal, generated at the phase-matching direction (-\(k_1+k_2+k_3\)) was picked up by another parabolic reflector and mixed with LO at a MCT detector (MCT10-010-E-LN4, ElectroOptical System INC) connected to a box-car integrator for heterodyne detection. The 2DIR measurements were performed by scanning the dephasing time \(\tau\), which is the delay time between \(k_1\) and \(k_2\), and the observation time \(t\), which is the delay time between \(k_3\) and LO. The 2D spectrum was constructed by a numerical two-dimensional Fourier transformation along both \(\tau\) and \(t\) directions.

Figure 3.6. (a) Functional scheme of a 2DIR setup. (b) Pulse sequence of 2DIR measurements.
3.6. IR-Perturbed TRIR Spectrometer

The IR-perturbed TRIR spectrometer was built based on the 2DIR setup described in Section 3.5. Additional UV excitation beam was introduced from another regenerative amplifier (Spitfire Pro, Spectra-Physics), which was seeded by the same Ti:sapphire oscillator. The fundamental laser output of this amplifier was frequency doubled using a BBO crystal to generate a 402 nm excitation beam. This UV beam was delayed by a translation stage of 600 mm long (Paker) and focused into the sample cell. Two mid-IR beams from the 2DIR setup were used, \( k_1 \) and \( k_3 \), with this UV beam resulted in a UV pump/mid-IR pump/mid-IR probe pulse sequence. Because the IR-perturbed TRIR technique measures the changes that mid-IR pump beam introduces to the TRIR spectra, the mid-IR pump beam was chopped at half the laser repetition rate, and the difference spectra was recorded with the mid-IR beam on and off. After passing through the sample, the mid-IR probe beam was dispersed by the monochromator and detected by the single channel MCT detector connected to the box-car integrator.

3.7. Fully Automated 2DIR Instrument

A block diagram of the essential components as well as the detailed optical scheme of the spectrometer is illustrated in Figure 3.7. A Ti:Sapphire laser, producing 1.5 W power at 1 kHz repetition rate, 800 nm wavelength, ca. 14 nm bandwidth (fwhm), and 80 fs pulse duration (Libra, Coherent), was used to pump a fully computer-controlled dual optical parametric amplifier (Palitra-duo, Quantronix). Two pairs of Signal and Idler OPA outputs were directed into two computer-controlled noncollinear difference-frequency generation (DFG) units (nIR-A and nIR-B, Quantronix), each featuring two interchangeable DFG crystals, AgGaS2 and AgGaSe2, to cover a broader range of mid-IR
frequencies. The mid-IR pulses energies produced by each DFG unit varied from 1.5 to 10 μJ, depending on the central wavelength. The 2DIR instrument features separate schematics for stabilizing the directions of both mid-IR beams, a unit to satisfy the phase matching conditions for the mid-IR beam directions at the sample, and interferometric delay measurement units with active phase stabilization and phase modulation. The heterodyned signal is measured using a multi-channel MCT array detector (IR-6400, Infrared Associates) attached to a monochromator (Triax-190, HORIBA).

**Figure 3.7.** Schematic of the dual-frequency 2DIR instrument. A. Essential functional components. B. Detailed optical schematic. Here Q is an MCT quad detector, D is an optical delay stage, T is a translation stage, PR is a parabolic reflector, Pr is a right-angled prism reflector, PZ is a gold mirror equipped with a piezo actuator, BS is a beam splitter, WP is a wave plate – wire-grid polarizer or two wire-grid polarizers assembly, GP is a wire-grid polarizer, W is a phase modulator (wobbler), F is a mechanical flipper, OM is an optical mask, PD is a Si photodiode, SC is a sample cell, IS is an image spectrometer, MCD is an MCT
array detector. BS1 is a 50/50 beam splitter with separate regions for m-IR and HeNe beams. Standard mirrors are omitted to increase legibility.

The 2DIR measurements were performed by scanning the delay between the first two pulses, \( \tau \), (both at the same central frequency) at a fixed waiting time, the delay between the second and third pulses, and recording the heterodyned spectrum in the frequency range of interest for every \( \tau \) (Figure 3.6B). Fourier transformation along the \( \tau \) direction results in a 2DIR spectrum. About 2-4 min is required to measure a single 2DIR spectrum. For RA 2DIR measurements, the waiting time, \( T \), was scanned and 2DIR spectra were recorded for each waiting time. It takes ca. 2 hours to measure typical waiting time dependence.

3.8. Computational Method

Calculations on the electronic ground states and the lowest energy triplet states of all related rhenium complexes were performed using the density functional theory (DFT) with a hybrid B3LYP hybrid functional.\(^9\) Characterization of low-lying singlet- and triplet-excited states (at Franck-Condon geometries and optimized geometries on potential surfaces) and normal mode analyses were carried out using time-dependent density functional theory (TDDFT). 6-31G** basis sets were used for C, H, O, and N atoms. LANL2DZ relativistic effective core potential and associated basis set was used for Re atom. Polarizable continuum model was employed to describe the solvent in ground state and excited state calculations. All the quantum chemical calculations were conducted using Gaussian 09 software package.\(^9\) Four types of charge population analysis were performed, including the Mulliken charge, the Lowdin charge, the NBO charge and the charge
population acquired from electrostatic potential fitting (the ESP charge), to determine the charge distribution of the corresponding electronic states. For all calculations, these four types of charge population analysis give qualitatively consistent results. Therefore, only the result of Mulliken charge will be presented and discussed.

For CHn compounds, their ground state structures and normal modes were calculated using DFT with B3LYP hybrid functional and 6-311++G(d,p) basis sets, as implemented in a Gaussian 09 software package.

3.9. Summary

The TRIR setup described in Section 3.4.2 was used for the excited state electron transfer study a series of rhenium complexes presented in Chapter 4 and Chapter 5. The IR-perturbed TRIR spectrometer (Section 3.6), as well as the fully automated 2DIR spectrometer (Section 3.7), was used in the electron transfer modulation experiments presented in Chapter 6. The fully automated 2DIR spectrometer (Section 3.7) was also mainly used in the study of ballistic energy transfer in oligomeric chain described in Chapter 7.

3.10. Acknowledgement

Support by the National Science Foundation (NSF, CHE-1090991) is gratefully acknowledged. The Louisiana Board of Regents (Grant No. LEQSF(2011-12)-ENH-TR-29) is thanked for supporting the acquisition of the fs Ti:Sapphire laser system.
Chapter 4. Evaluating the Charge Transfer Extent in the Excited States of Rhenium(I) Complexes

The work presented in this chapter has been published in the following paper:


4.1 Overview

The mechanism of photoinduced intramolecular electron transfer (ET) has been the subject of intensive study for more than 30 years.\textsuperscript{92-98} Since photoinduced ET begins with light absorption, the electron-density distribution and degree of charge transfer associated with the initially formed and relaxed excited states are critical, but are often poorly characterized. For transition metal complexes with metal-to-ligand charge transfer (MLCT) excited states, the structural and charge polarization changes that follow from the initial excitation to the generation of the intramolecular photoredox products can be subtle.\textsuperscript{94, 99-100} This is especially true when the free energy of the charge-separated state formed upon electron transfer is structurally similar to that of the initial excited state. Formation of an intramolecular charge separated state may occur in discrete steps (i.e., initial formation of a MLCT excited state may be followed by an intramolecular electron-transfer step leading to polarization of charge from D to A) or absorption may directly create an excited electronic state with a significant admixture of the charge-separated DA product that then
further relaxes. Distinguishing between these two closely related pathways requires a spectroscopic approach that provides direct temporal information on the electron-density distribution. The ability to evaluate the degree of state mixing using a direct spectroscopic approach may allow the correlation of the donor-acceptor interaction with the full course of the reaction on the excited manifold.

Rhenium tricarbonyl-diimine complexes, \([\text{Re}^1(\text{CO})_3(N,N)(L)]^{+0}\) (+ when \(L\) is a neutral ligand with a substituent capable of electron donation to the excited complex), are appealing candidates to dissect the charge-transfer evolution as a function of time after excitation because infrared modes of the carbonyl and imine ligands provide direct probes of charge localization. Recent studies of Vlcek\(^\text{25, 31, 101-102}\) and others provide insight into the vibrational relaxation of the MLCT states of \([\text{Re}^1(\text{CO})_3(N,N)(L)]^{+0}\) complexes, where \(L\) = pyridine or chloride. In these complexes, the lowest energy metal to ligand charge transfer (MLCT) state is directly or indirectly prepared by optical excitation.\(^\text{26, 102-105}\) Picosecond time-resolved changes in the CO stretching mode frequencies of the complexes indicate that formation of the vibrationally relaxed \(^3\text{MLCT}\) state in halocarbon solvents occurs with time constants in the range of 1-10 ps. Vleck and others used ps time-resolved infrared (TRIR) spectroscopy to follow the dynamics of intramolecular energy and electron transfer in rhenium carbonyl systems with well-defined charge-separated states.\(^\text{27, 106-110}\)

In the regime of small driving force, light-induced ET dynamics can be controlled by the solvent medium. Using time-resolved UV-VIS methods, Schanze and coworkers explored the photophysics of \([(\text{bpy})\text{Re}^1(\text{CO})_3(4\text{DMABN})]^+\) (4DMABN = 4-dimethylamino-benzenitrile) in solvents ranging from pure methylene chloride (DCM) to pure acetonitrile (AN) in polarity. Luminescence results indicated strong, long lived (\(\sim 1\mu s\)
emission from the complex in DCM and comparisons to [(bpy)Re\(^{1}(CO)\(_{3}(AN)\)]\(^{+}\) (AN=acetonitrile) indicated that the emitting excited state is a Re(d\(\pi\)) to bpy(\(\pi^{*}\)) MLCT state. Increasing the mole fraction of acetonitrile in mixed solvents caused the emission quantum yield to decrease nearly to zero and caused the lifetime to decrease to less than 1 ns for the 4DMABN complex. This behavior was attributed to the formation of a 4DMABN to bpy interligand charge transfer (LLCT) state ( [(bpy\(^{-}\))Re\(^{1}(CO)\(_{3}(4DMABN^{+})\)]\(^{+}\) ) that rapidly relaxes to the ground state. The LLCT state was postulated to form via initial excitation of a MLCT state followed by intramolecular electron transfer to produce the LLCT state. The relative energies of the MLCT and LLCT states were suggested to interchange on changing the solvent from DCM to DCM/AN mixtures. The observed behavior (including ps time-resolved visible spectroscopy) is consistent with the model.\(^{109}\)

![Scheme 4.1. Structures of the ReBN, Re4DMABN, and Re3DMABN compounds](image)

Here, we use time-resolved infrared (TRIR) and UV-VIS spectroscopies as well as DFT and TDDFT computations to probe [(bpy)Re\(^{1}(CO)\(_{3}(4DMABN)\)]\(^{+}\) (Re4DMABN) and the related complex with a 3-dimethylamino-benzenitrile ligand (Re3DMABN) (Scheme 4.1). The results indicate that despite similarity of the redox properties of the two complexes and their excited-state lifetime solvent dependence, the nature of the excited states involved...
differs drastically. For example in DCM, Re4DMABN has a metal-ligand (Re-4DMABN) to ligand (bpy), MLLCT state, while the 3IL state is lowest in energy for Re3DMABN. In MeOH/DCM (1:1) mixed solvent the lowest energy state for Re4DMABN is (4DMABN$\rightarrow$bpy) LLCT, although it is a MLLCT state for Re3DMABN. Definitive assignment was only possible by considering all available data, which include TRIR spectral data with numerous IR labels, fluorescence lifetime measurements, triplet quenching results, and DFT computations. A simple three-state coupling model is presented to describe the states formed in both compounds in the two solvent systems.

4.2. Experimental Details.

4.2.1. Femtosecond Spectroscopy.

Detailed description of the 3 pulse time-resolved spectrometer is presented in Chapter 3.4.2.

4.2.2. Nanosecond Spectroscopy.

Transient absorption spectra in the UV and visible spectral regions were obtained by collecting transient decays at 10 nm intervals following pulsed laser excitation using a system involving an Applied Photophysics LKS 60 optical system/software and a Quantel Brilliant laser equipped with second and third harmonics and an OPOTEK OPO (420-670 nm) for tunable excitation. The excitation wavelength used for these complexes was 420 nm. Samples were degassed with N$_2$ for 20 minutes prior to acquisition of transient decays.

4.2.3. Cyclic Voltammetry.

Voltammograms were obtained using a CH Instruments CH1730A Electrochemical Analyzer. The working electrode was a glassy-carbon electrode, the counter electrode was a Pt wire, and the reference electrode was an aqueous Ag/AgCl electrode. Data were
collected in acetonitrile and dichloromethane solutions containing 0.1M TBAPF$_6$. All samples were bubble degassed with argon for 10 minutes prior to collection.

4.2.4. Complex Synthesis and Sample Preparation

Toluene, methylene chloride, and hexane were purchased from PHARMCO-AAPER. [Re(CO)$_5$Cl] was purchased from Strem Chemical. 3-aminobenzonitrile, 2,2’-bipyridine, paraformaldehyde, and sodium cyanoborohydride were purchased from Sigma Aldrich. Benzonitrile and 4-dimethylaminobenzonitrile were purchased from Alfa Aesar. All synthetic materials were used as received other than 3-aminobenzonitrile which was N-methylated using a published literature method.$^{111}$ The complexes [Re(bpy)(CO)$_3$(L)](BARF) (L = BN, 3DMABN, 4DMABN; BARF = Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) were prepared according to modifications of literature methods.$^{111-113}$ The purity of the compounds was evaluated by $^1$H NMR and MALDI TOF mass spectrometry. Synthetic details, NMR spectra, MALDI spectra and ORTEP representations are described in the dissertation of Dr. Tod Grusenmeyer.$^{114}$ NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. MALDI spectra were obtained on a Bruker Autoflex III time of flight mass spectrometer. All UV-VIS absorption spectra were measured on a Hewlett-Packard 8452 diode array spectrophotometer. Luminescence spectra were obtained using a PTI scanning spectrofluorimeter.

Sample solutions for transient infrared experiments: solutions of 20 mM concentration were prepared in two solvents: pure dichloromethane (DCM) and methanol/DCM mixture (1:1 by volume), referred here as MeOH/DCM solvent. The spectroscopic grade solvents (Aldrich) were used as received. To avoid influence of sample degradation over laser excitation, the time-resolved measurements were performed
in the flow cell (DLC2, Harrick) with an optical path length of 150 µm at 23.5 ± 0.5 °C. The IR spectra of the sample before and after the experiment differ by less than 10%.

4.2.5. Quantum chemistry calculations

Detailed quantum chemistry method is presented in Chapter 3.8.

4.3 Results and Discussion

4.3.1. Synthesis and Structural Characterization

The complexes studied were readily prepared using [(bpy)Re(CO)3(OTf)] (OTf = triflate) by reaction with the benzonitrile ligand and metathesis of the resulting triflate salt with the NaBARF, precipitating sodium triflate. Synthetic details, characterization of the complexes, including proton NMR, MALDI mass spectra and single crystal structure data are described in the dissertation of Dr. Tod Grusenmeyer. Crystal structures of the three complexes indicate only small differences among them in bond distances (< 20 pm) and angles for the Re, CO ligands and bpy ligand; selected bond distances and angles are given in Table 4.1. The three

| Table 4.1. Selected bond lengths and bond angles obtained from single crystal structures of the [Re(bpy)(CO)3L] (BARF) complexes (in Å). |
|---------------------------------|------------------|------------------|---------------|
|                                  | Re4DMABN         | Re3DMABN         | ReBN          |
| Nitrile Information             |                  |                  |
| Re-N (nitrile) bond length      | 2.134(4)         | 2.124(2)         | 2.108(8)      |
| CN bond length                  | 1.144(6)         | 1.150(3)         | 1.14 (1)      |
| C(phenyl)-C(nitrile) bond length| 1.424(6)         | 1.435(3)         | 1.43 (1)      |
| C(phenyl)-N(dimethyl) bond length| 1.363(6)         | 1.372(4)         |               |
| Re-N-C (NITRILE) angle          | 174.29           | 177.68           | 178.27        |
| Bipyridine Information          |                  |                  |
| Average Re-N(bpy) bond length   | 2.167 (3)        | 2.171 (2)        | 2.172 (7)     |
benzonitrile ligands (BN, 3DMABN and 4DMABN) also exhibit only minor differences in the Re-N and NC bond lengths; the bond angles and lengths in the phenyl ring also change very little among the three complexes. For both of the DMABN ligands, the Re-N (nitrile) bond length is slightly longer than that for the BN ligand. This observation, taken together with the fact that the bond length of the Re-C (CO) _trans_ to the DMABN ligand is shorter than for the BN complex and the _trans_ CO bond length is longer, suggests that electron donation from the dimethylamine substituent diminishes the Re–nitrile back bonding interaction and increases the backbonding to the _trans_ CO in the electronic ground state. This trend is also reflected in the infrared spectra of the complexes (*vide infra*).
4.3.2. UV-VIS Absorption Spectra, Luminescence Spectra, and Transient Absorption.

Figure 4.1 shows that the UV-VIS absorption spectra of ReBN and Re3DMABN in dichloromethane (DCM) have maxima at ca. 320 nm and are assigned to bpy-localized $\pi$-$\pi^*$ transitions \(^{115}\) while Re4DMABN has a unique strong absorption at 334 nm with a relatively high molar absorptivity that, by comparison with the 4DMABN ligand, is clearly an intraligand amine to nitrile charge transfer transition (ILCT).\(^{115}\) Weaker broad absorption transitions from 320 to 430 nm were assigned to $d\pi$(Re)$\rightarrow$$\pi^*$ (bpy) MLCT transitions based on earlier observations.\(^{105, 116-118}\) Vertical excitation calculations using TDDFT predicted that the MLCT transitions are at ca. 379, 372, and 385 nm in ReBN, Re4DMABN and Re3DMABN, respectively. For Re4DMABN, the vertical excitation energy of S1, S2, T1 and T2 are 476 nm, 372 nm, 481 nm and 441 nm, respectively. The nature of these states at the Franck-Condon geometry are LLCT, MLCT, LLCT and ILCT, respectively. The oscillator strength of S2 is 0.0137 while that of S1 is 0.0020. For Re3DMABN, the vertical excitation energies and nature of the states for S1, S2, T1 and T2 are 494 nm (LLCT), 387 nm (ILCT), 514 nm (LLCT) and 494 nm (ILCT), respectively. The MLCT states according to TDDFT calculations are from S3 to S5 with energies of 385 nm, 361 nm, 352 nm, and the corresponding oscillator strengths are 0.0043, 0.0894 and 0.0531. The oscillator strengths of S1 and S2 are 0.0001 and 0.0531. The computed electronic spectrum agrees well with experiments.
All three complexes exhibit luminescence in DCM at room temperature, and spectra are shown in Figure 4.2 for emission in DCM and MeOH:DCM (1:1). Emission maxima, luminescence quantum yields and excited-state lifetimes are given in Table 4.2. Based on previous literature reports\textsuperscript{109} and computational results described here (\textit{vide infra}), the yellow luminescence from the ReBN complex is from the Re(dπ)→bpy(π*) MLCT state. The similarity of the observed emission maximum and line shape of the DMABN complexes suggests that the emission originated in MLCT transitions. However, the 3DMABN complex differs from the other two in that the emission is very weak in DCM.

A striking feature of Re3DMABN

**Table 4.2.** Luminescence maxima, quantum yields and lifetimes of the complexes in aerated DCM and MeOH/DCM (1/1) at room temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>ReBN</th>
<th>Re3DMABN</th>
<th>Re4DMABN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>DCM</td>
<td>MeOH/DCM</td>
<td>DCM</td>
</tr>
</tbody>
</table>

**Figure 4.2.** Luminescence spectra of the complexes in aerated DCM (solid lines) and in MeOH/DCM (dashed lines) at room temperature. The spectra in MeOH/DCM were scaled to match those in DCM by the factors indicated in the inset.
is that the lifetime of the weak luminescence is more than a factor of 30 longer than the measured lifetime of the other two complexes. This very long lived and weak luminescence suggests that the emitting excited state is not MLCT in origin. The possibility of impurity luminescence in the 3DMABN complex can be ruled out by the observation of a long lived transient absorption (Figure 4.3).

All of the complexes have excited state UV-VIS absorbance between 400 and 450 nm, which parallels the results of Schanze et al. for Re4DMABN in mixed DCM/CH₃CN solutions.¹⁰⁹ The BN and 4DMABN complexes exhibit bleaching at longer wavelengths that result from the luminescence of these complexes. Despite similarities among the transient spectra of the long-lived states in the three compounds (Figure 4.3), it is very likely that the equilibrated excited state of the Re3DMABN complex differs from the others since its radiative decay rate (Table 4.2) is nearly a factor of 1000 slower than the BN and 4DMABN complexes.
Figure 4.3. Nanosecond transient absorption spectra of ReBN, Re3DMABN, and Re4DMABN in DCM at room temperature at the delay times indicated. Strong luminescence observed for the ReBN and Re4DMABN complexes in the 480-690 nm range is not shown (appearing as negative absorbance).

Upon changing the solution to the more polar MeOH/DCM (1:1) mixture, all of the complexes exhibit weaker luminescence and shorter excited-state lifetimes. The magnitude of the change is much more pronounced in the two DMABN complexes. In the two DMABM complexes, the luminescence and transient absorbance lifetimes decrease by a factor of >100 in the mixed solvent, as compared to a factor of 1.6-3 for ReBN. In Re3DMABN, the excited state lifetime in DCM is more than 30 times larger than that of either of the other complexes, but decreases precipitously in the mixed solvent, from 25-30 µs in DCM to 30 ns in MeOH/DCM. The ReBN and Re3DMABN complex spectra were essentially the same as those in DCM, with shorter lifetimes, as reported in Table 4.2. Such excited-state lifetime decreases in more polar solvents are often associated with the existence of strongly polarized excited states, which are higher in energy in nonpolar solvents but are stabilized in polar solvents and provide additional relaxation pathways to
the ground state. Such polarized states could be either ligand-to-ligand charge separated states (LLCT), [((bpy−)Re(CO)3(DMABN+)−)]+ or highly polarized ligand-based states.

4.3.3. Electrochemistry

Cyclic voltammetry measurements on the complexes exhibit waves attributable to one-electron reduction and oxidation in DCM and CH3CN solutions (Table 4.3). Here, CH3CN was used in place of CH3OH since it was not possible to obtain voltammetric data in CH3OH because of competing solvent redox processes. The observed waves at positive potentials in the voltammograms of both of the DMABN complexes occur more than 0.5 V more negative than the first oxidation of the ReBN complex (\(E^0(\text{Re(II)/Re(I)})\), and are clearly associated with oxidation of the dimethylamine substituent.\(^{119}\) The oxidation is quasi-reversible in acetonitrile, suggesting that the cation radical reacts irreversibly within a few seconds of being formed (sweep rates were 0.1 Vs\(^{-1}\)). In addition, oxidation in DCM is observed at more positive potentials than in CH3CN. Reductive voltammograms in CH3CN are reversible, and reductive waves occur at nearly the same potential for all three complexes. The reductive behavior in DCM is irreversible, but cathodic peaks are clearly observed for both the DMABN complexes. These data are included in Table 4.3. The difference between \(E^0(\text{2+/+})\) and \(E^0(+/0)\) provides an approximate value for the energy of the charge separated species, [((bpy−)Re(CO)3(DMABN+−))]−; the values of \(\Delta E_{CS}\), shown in Table 4.3, are well in excess of 2 V, suggesting that back electron transfer from this state may reside in the Marcus inverted region. The emission maxima have energies at least 0.1 V lower than the estimated charge-separated states in each case and, while the true excited state energies will be somewhat higher, it is clear that the free energies for intramolecular electron transfer reaction will be close to zero.
Table 4.3. Redox potentials (in V) for the complexes in DCM and CH$_3$CN vs. Ag/AgCl and free energies of the charge separated states.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E^0(2+/+)$, ($\Delta E_p$, V) in DCM</th>
<th>$E^0(2+/+)$, ($\Delta E_p$, V) in CH$_3$CN</th>
<th>$E^0(+/-)$, ($\Delta E_p$, V) in DCM</th>
<th>$E^0(+/-)$, ($\Delta E_p$, V) in CH$_3$CN</th>
<th>$\Delta E_{CS}$, V in DCM (in CH$_3$CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CO)$_3$Re(bpy)(BN)]$^+$</td>
<td>&gt; 1.5</td>
<td>&gt; 1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[(CO)$_3$Re(bpy)(3DMABN)]$^+$</td>
<td>1.28 (0.24)</td>
<td>1.17 (0.14)</td>
<td>-1.13</td>
<td>-1.17 (0.08)</td>
<td>2.41 (2.34)</td>
</tr>
<tr>
<td>[(CO)$_3$Re(bpy)(4DMABN)]$^+$</td>
<td>1.43 (0.09)</td>
<td>1.27 (0.07)</td>
<td>-1.16</td>
<td>-1.16 (0.08)</td>
<td>2.59 (2.43)</td>
</tr>
</tbody>
</table>

4.3.4. Infrared Absorption Spectra

Vibrational absorption spectra of the three compounds feature several characteristic peaks that are readily assigned (Figure 4.4, Table 4.4). The strongest peaks at ca. 2040 and ca. 1945 cm$^{-1}$ belong to the symmetric and asymmetric stretching modes of the three carbonyl ligands, respectively.$^{108}$ Notice that the much broader peak at ca. 1945 cm$^{-1}$ consists of two $\nu_{as}$(CO) transitions.$^{108}$ The relatively weak peak around 2250 cm$^{-1}$ belongs to the C≡N stretching mode. Two additional peaks of interest are apparent in the 1600-1615 cm$^{-1}$ region for all three compounds. DFT calculations indicate that the two vibrational transitions between 1600 and 1615 cm$^{-1}$ correspond to the symmetric ring stretching mode of the bpy, $\nu_{ss}$(bpy), and a stretching motion of the phenyl ring of DMABN (or BN), $\nu_{ss}$(Ph) (Table 4.4). The weaker absorption peak, that appears at approximately a constant frequency of 1612 cm$^{-1}$, is assigned to $\nu_{as}$(bpy), while the lower-frequency peak at ca. 1604 cm$^{-1}$ has different IR intensities in the different compounds (Table 4.4), and is assigned as
$\nu_{ss}(\text{Ph})$. The DFT calculations suggest only a minor mixing of these two modes that does not exceed $\sim5\%$. Interestingly, not only is the $\nu_{ss}(\text{Ph})$ peak in $\text{Re4DMABN}$ much stronger than that of $\nu_{ss}(\text{bpy})$, but its extinction coefficient is comparable to that of the $\nu(\text{CO})$ transitions. Note that the $\nu_{ss}(\text{Ph})$ mode involves symmetric stretching motion of the phenyl ring along the long axis of the ligand and its IR intensity is strongly dependent of the ligand polarization.

![Figure 4.4](image.png)

**Figure 4.4.** Linear absorption spectra of the three compounds in DCM and MeOH/DCM. The baselines for two of them are shifted by 0.4 and 0.8 for clarity. The spectra in the right panel were scaled by 5-fold (thick lines), while thin lines show unscaled spectra.

The stretching frequency of the metal coordinated CO is known to be sensitive to the metal center’s charge,$^{26-27}$ a result of $\pi$ backbonding from the metal influencing the CO bond order. The fact that the CO absorption peaks for these complexes show only small differences in both their central frequencies and their IR intensities suggests that the ground state charge of Re is similar in all three complexes.

**Table 4.4.** Experimental and DFT computed ground-state vibrational frequencies (in cm$^{-1}$) of several characteristic modes for the three compounds in DCM.
Larger differences between the three complexes are found in the C≡N stretching region. While the CN frequencies for ReBN and Re3DMABN are similar, there is a striking 24 cm$^{-1}$ shift of $\nu$(CN) to lower frequencies in Re4DMABN. In addition, the IR intensity of $\nu$(CN) in Re4DMABN is more than 3-fold larger than in the other complexes. These differences suggest that the 4DMABN ligand, but not 3DMABN or BN, significantly affects the electron density distribution in the complex’s ground electronic state. The main electron distribution differences occur in the L-ligand region and on the neighboring groups, as can be seen from the Re-N (nitrile) and Re-C (CO trans to nitrile) bond lengths as well as from the in Re-N-C angle (Table 4.1). This is further supported by the DFT computations (Table 4.5).

Table 4.5. Calculated Mulliken charges for the ground state (S0) and the lowest energy triplet state (T1) in DCM and in water and the charge changes (T1-S0).
<table>
<thead>
<tr>
<th>Functional group</th>
<th>In DCM</th>
<th>In water</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0, T1, T1-S0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### ReBN

<table>
<thead>
<tr>
<th></th>
<th>bpy</th>
<th>BN</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
<th>bpy</th>
<th>BN</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0, T1, T1-S0</td>
<td>0.53, 0.27, -0.26</td>
<td>0.19, 0.21, +0.02</td>
<td>0.37, 0.39, 0.02</td>
<td>-0.18, -0.18, 0.00</td>
<td>0.63, 0.73, +0.10</td>
<td>-0.35, -0.21, +0.14</td>
<td>0.53, 0.34, -0.19</td>
<td>0.19, 0.21, +0.02</td>
<td>0.37, 0.38, 0.01</td>
<td>-0.18, -0.17, 0.01</td>
<td>0.63, 0.71, +0.08</td>
<td>-0.35, -0.26, +0.09</td>
</tr>
</tbody>
</table>

### Re3DMABN

<table>
<thead>
<tr>
<th></th>
<th>bpy</th>
<th>3DMABN</th>
<th>DMA</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
<th>bpy</th>
<th>3DMABN</th>
<th>DMA</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0, T1, T1-S0</td>
<td>0.52, 0.50, -0.02</td>
<td>0.18, 0.28, +0.10</td>
<td>0.52, 0.72, +0.20</td>
<td>-0.14, -0.09, +0.05</td>
<td>-0.20, -0.35, -0.15</td>
<td>0.62, 0.60, -0.02</td>
<td>-0.34, -0.40, -0.06</td>
<td>0.53, 0.51, -0.02</td>
<td>0.18, 0.20, +0.10</td>
<td>0.52, 0.73, +0.20</td>
<td>-0.14, -0.08, +0.06</td>
<td>-0.20, -0.35, -0.16</td>
<td>0.62, 0.61, -0.02</td>
<td>-0.34, -0.42, -0.06</td>
</tr>
</tbody>
</table>

### Re4DMABN

<table>
<thead>
<tr>
<th></th>
<th>bpy</th>
<th>4DMABN</th>
<th>DMA</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
<th>bpy</th>
<th>4DMABN</th>
<th>DMA</th>
<th>Ph</th>
<th>CN</th>
<th>Re</th>
<th>3 CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0, T1, T1-S0</td>
<td>0.52, -0.15, -0.67</td>
<td>0.22, 0.64, 0.42</td>
<td>0.00, 0.17, 0.17</td>
<td>0.45, 0.70, 0.25</td>
<td>-0.23, -0.23, 0.00</td>
<td>0.62, 0.73, 0.11</td>
<td>-0.36, -0.23, 0.13</td>
<td>0.53, -0.20, -0.73</td>
<td>0.22, 0.82, 0.60</td>
<td>0.00, 0.24, 0.24</td>
<td>0.45, 0.78, 0.33</td>
<td>-0.23, -0.2, 0.02</td>
<td>0.62, 0.70, 0.08</td>
<td>-0.37, -0.31, 0.06</td>
</tr>
</tbody>
</table>

### 4.3.5. Transient Infrared Spectroscopy

In an effort to understand the differences in the characteristics of the excited states for the three complexes, TRIR spectra were measured in the spectral regions of the CO
(1900 to 2150 cm\(^{-1}\)), CN (2150 to 2310 cm\(^{-1}\)), and ring (1540 to 1640 cm\(^{-1}\)) vibrations. The transient spectra represent the differences between the vibrational spectra in the excited and ground electronic states; positive peaks belong to absorption by modes of the excited states and negative peaks are due to bleaching of ground electronic state modes. TRIR spectra in the CO stretching region were previously reported for a variety of rhenium tricarbonyl\(^{26-27}\), \(^{30, \, 103-104, \, 120}\) and other transition metal complexes, and a general understanding of the associated spectral changes has been reached. Removal of electron density from the metal in Re-to-bpy MLCT transitions leads to a decrease of the Re(d\(\pi\)) backbonding to the \(\pi^*\) orbitals of CO ligands and to an increase of the CO stretching frequencies.\(^{28}\) Conversely, decreases of the CO frequencies indicate an increase of electron density at the metal.

**ReBN in DCM: Long-lived MLCT State is Formed.** The TRIR of ReBN in DCM is shown in Figure 4.5. The early-time transient spectra of the CO modes following 402 nm excitation of ReBN are characteristic of MLCT state formation.\(^{28}\) The two \(v_{as}(CO)\) peaks that overlap in the ground state are well resolved in the excited state, with the maxima at small delay times of 1976 and 2017 cm\(^{-1}\). The large frequency increase of all three CO peaks observed instantaneously upon excitation, +64 (as\(_1\)), +30 (as\(_2\)), and +11 cm\(^{-1}\) (ss), is in accord with formation of a Re(d\(\pi\))\(\rightarrow\) (\(\pi^*\))bpy MLCT state. (The dynamics occurring faster than the instrument response time of ca. 200 fs is described as instantaneous.) The excited-state absorption peaks show dynamics with a characteristic time of ca. 17 ps (Figure 4.5), which results in a further shift to higher frequencies of all three CO peaks by +5 (as\(_1\)), +6 (as\(_2\)), and +2.5 cm\(^{-1}\) (ss), peak narrowing, as well as growth of the \(v_{as}(CO)\) and \(v_{as1}(CO)\) peak amplitudes (Figure 4.5). Importantly, the excited state relaxation does not lead to recovery of the ground electronic state vibrational frequencies, as the bleaching peaks do
not diminish in intensity. Such dynamics can be assigned to a combination of solvation, vibrational cooling, and electronic relaxation among different excited states.\textsuperscript{27, 121-122} There is considerable evidence in the literature to indicate that the electronic relaxation to the lowest triplet MLCT state in complexes with heavy metals such as Re occurs within several hundred femtoseconds.\textsuperscript{30-31} The solvation process in DCM is very fast with the slowest solvation component reported at 1.0 ps.\textsuperscript{123} Thus, vibrational cooling remains the most likely cause of the observed dynamics.\textsuperscript{27} Vibrational relaxation to the lowest MLCT state following 402 nm excitation deposits ca. 6000 cm\textsuperscript{-1} (using the luminescence peak at 524 nm) of excess energy into the complex within the first few hundred femtoseconds after excitation, resulting in excitation of a range of vibrational modes in the complex. Anharmonic coupling of these modes with the CO modes causes frequency shifts of the latter.\textsuperscript{87, 121-122, 124-125} Thus, cooling of the complex causes the CO peaks to narrow and shift to higher frequencies. A thermalization time in a nonpolar solvent under similar concentration and excitation conditions was previously found to be ca. 20 ps using relaxation-assisted 2DIR spectroscopy.\textsuperscript{124} The CO modes are clearly the most sensitive to the excess energy, possibly because of a large dipole-dipole contribution to their interaction energy with the other modes in the complex.
Figure 4.5. Transient infrared spectrum of ReBN in DCM following 402 nm excitation. Insets show kinetics measured at indicated frequencies and their fits to a single exponential function. The arrows indicate the directions of the spectral changes in the excited state.

There is a small instantaneous shift of the CN mode frequency of ca. -10 cm\(^{-1}\) upon electronic excitation; in addition, the CN transition dipole in the excited state increases \(\sim 4\) fold. Apparently, the ps excited-state dynamics affecting the CO modes does not perturb the CN mode, confirming that the BN ligand is not involved significantly in the MLCT transition and that the ground state back-bonding to the CN is much less than that for the CO ligands. Results of DFT calculations support the formation of the Re \((d\pi) \rightarrow \text{bpy}(\pi^*)\) transition. The calculated changes in Mulliken charges (Table 4.5) between the ground and excited state indicate little change on the nitrile ligand, as well as formation of a positive charge on the Re and CO ligands and negative charge on the bpy. No further spectral changes beyond 50 ps are found for ReBN in the 430 ps time window; the overall excited state lifetime of \(\sim 0.8 \mu\text{s}\) is attributed to the lifetime of MLCT state of ReBN.

Re4DMABN in DCM: Despite Long Lifetime, the Lowest Energy Excited State is Different than in ReBN. The TRIR spectra of Re4DMABN in DCM in the CO region are
similar to those of ReBN, implying that a similar MLCT state is formed upon excitation (Figure 4.6A). However, in contrast to ReBN, the CN mode in Re4DMABN decreases in frequency by 46 cm$^{-1}$ in the excited state and exhibits a large increase in intensity, indicating a change of the CN bond order toward a double bond limit. Assuming that the stretch at this frequency is truly CN localized in both ground and excited states, the ratio of the ground to excited state force constants is 1.04; computational results yield different values of the absolute stretching frequencies, but the relative change in the force constant is the same for both the S1 and T1 states. In addition, the $\nu_{ss}(\text{Ph})$ peak at 1604 cm$^{-1}$ (Table 4.4), shows a 10 cm$^{-1}$ decrease in frequency (Figure 4.6A), indicating electron density redistribution in the 4DMABN ligand core in the excited state.

Notice that a large change in the CN and Ph stretch frequencies of the 4DMABN ligand is expected if partial oxidation of the dimethyl amino moiety occurs. The observed spectral changes reveal that the state formed within the first 200 fs features an increase in the negative charge on the Re center and significant changes in electron distribution in the 4DMABN ligand. The resulting state can be viewed as having “mixed” triplet metal-ligand (DMABN) to ligand (bpy) charge transfer character (i.e., MLLCT).

Further, only small spectral changes occur over the first 50 ps for all the modes examined (Figure 4.6A), and no further changes are observed between 50 and 430 ps. Relaxation times of ca. 2.7 ps and ca. 18 ps are observed. Because both time components are much slower than the solvation time of DCM$^{123}$ and peaks shift to higher frequencies and narrow, the dynamics are assigned primarily to vibrational cooling of the complex, as with the ReBN complex. No further dynamics beyond 50 ps are found for Re4DMABN in DCM in the 430 ps time window for all vibrational peaks studied. Interestingly, despite
the similarities in luminescence and transient absorption spectra and dynamics in the visible spectral region between Re4DMABN and its parent compound ReBN, the transient infrared spectra clearly indicate significant electron density redistribution of the coordinated 4DMABN ligand.

**Figure 4.6.** Transient infrared spectra of Re4DMABN in (A) DCM and (B) MeOH/DCM following 402 nm excitation. Insets show kinetics measured at indicated frequencies together with a single exponential fit (if two time components are shown). The arrows indicate the directions of the spectral changes in the excited state.
Re4DMABN in MeOH/DCM: Equilibrium of LLCT and MLLCT States. The transient IR spectra of Re4DMABN in MeOH/DCM at small delay times (<1ps) are similar to those in pure DCM (Figure 4.6B) for all modes studied. Instantaneous shifts to lower frequency of \( \nu(CN) \) and \( \nu_{as}(Ph) \) suggest prompt formation of the MLLCT excited state. Notice that the width of the CN peak in the excited state in MeOH/DCM (ca. 44 cm\(^{-1}\)) is substantially larger than that in DCM (ca. 33 cm\(^{-1}\)), indicating increased inhomogeneity of CN environment in a more polar solvent.

The excited-state evolution of Re4DMABN in MeOH/DCM shows similarities with the behavior in DCM in the first few ps: the upward frequency shift and narrowing of the CO peaks, small growth of the CN peak all occur with a characteristic time of ca. 3 ps (Figure 4.6B). These dynamics clearly involve vibrational cooling but also can be influenced by solvation. The solvation dynamics in MeOH have two slow components, of 3.2 (30%) and 15.3 ps (26%);\(^{123}\) the former can contribute to the observed spectral changes with a ca. 3 ps characteristic time. In addition to the relatively fast cooling-solvation process, a new process with a characteristic decay time of ca. 70 ps is found for all studied modes of Re4DMABN in the mixed MeOH/DCM solvent. This relaxation causes a downshift of all three CO frequencies, which for \( \nu_{as2}(CO) \) is apparent from the increased absorbance at ca. 1910 cm\(^{-1}\), accompanied by a bleach cancelation at ca. 1935 cm\(^{-1}\), as well as by a substantial decrease of the \( \nu_{ss}(CO) \) transition dipole, indicating that the changes are associated with an increase of the negative charge at the metal center. Concomitantly, the \( \nu(CN) \) and \( \nu_{as}(Ph) \) peaks decrease by factors of 1.65 and 2.1, respectively. No new CN spectral region peaks were found as a result of the peak decay at 2190 cm\(^{-1}\), which likely
indicates that a new peak formed is weak and broad. The 70 ps decay of the peak at 1595 cm\(^{-1}\) leads to the formation of a weaker peak at 1555 cm\(^{-1}\) (Figure 4.6B, inset).

**Figure 4.7.** Time resolved IR spectra of Re3DMABN in (A) DCM and (B) MeOH/DCM following 402 nm excitation. The insets show kinetics and zoomed in transient spectra.

The 70 ps process is too slow to be associated with solvation or cooling; solvent facilitated structural rearrangements of the complex or electronic relaxation could be responsible for it. Only partial conversion of ca. 52% from the MLLCT state to the new
state is found. Compared to the MLLCT state, the new state is characterized by increased electron density at Re, significant reduction of the $v_{ss}(\text{Ph})$ frequency, and high electronic asymmetry for the three Re-N directions (large splitting of the two $v_{as}(\text{CO})$ modes), suggesting substantial 4DMABN→bpy character (denoted as LLCT vide infra; Figure 4.8). Based on the amplitude of the changes (ca. 52%) of the $v_{ss}(\text{Ph})$ amplitude, the LLCT state is slightly lower in energy than the MLLCT state that is well characterized in DCM. It is suggested that the LLCT state is responsible for the greatly enhanced excited state relaxation rate in the mixed solvent.  

*Formation of the LLCT state is apparent in TRIR spectral changes of some vibrational modes ($v_{ss}(\text{Ph})$), while the other modes (CN) show only little changes.*

**Re3DMABN in DCM: Long-lived $^3$IL State is Formed.** Upon electronic excitation, the CO frequencies of Re3DMABN shift upward in accord with formation of an MLCT state (Figure 4.7A). The frequency shift values, $+70$ (as$_1$), $+30$ (as$_2$), and $+17$ cm$^{-1}$ (ss), are the largest among all three compounds, suggesting preparation of a larger positive charge on the Re in Re3DMABN. The CN peak is shifted to lower frequencies upon excitation. The shift of $-12$ cm$^{-1}$ (Figure 4.7A), which is larger than is found in ReBN (-10 cm$^{-1}$) but much smaller than is found in Re4DMABN (-50 cm$^{-1}$), suggests that the excited state in Re3DMABN has mostly MLCT character. Only a bleach signal is found for the $v_{ss}(\text{Ph})$ mode at small time delays. Detailed analysis of the averaged transient spectra (Figure 4.7A inset, red line) indicates a bleach-peak cancelation on the low-frequency side of the peak, demonstrating that a new absorption peak is centered at ca. 1594 cm$^{-1}$ (red arrow) and that the transition dipole of this mode in the excited state is reduced. Small frequency shifts of
the $\nu_{ss}(\text{Ph})$ and $\nu(\text{CN})$ confirm that the initially prepared excited state is predominantly a MLCT (Re$\rightarrow$bpy) state.

The excited state of Re3DMABN in DCM shows unique spectral changes occurring with a characteristic time of ca. 20 ps: the three CO peaks shift to lower frequencies by -26 cm$^{-1}$ ($\text{as}_1$ and $\text{as}_2$) and -12 cm$^{-1}$ (ss) with respect to the ground state frequencies. The modes $\nu(\text{CN})$ and $\nu_{ss}(\text{Ph})$ shift to lower frequencies by -127 and -66 cm$^{-1}$, respectively, indicating a large change of the 3DMABN charge distribution. The peak growth at 1535, 1920, 2029, 2132, and 2132 cm$^{-1}$ occurs concomitantly with the decay at 1594, 1980, 2015, 2062, and 2250 cm$^{-1}$ with the characteristic time of ca. 20 ps. What is the nature of this excited state? The down shift of the CO frequencies is formally consistent with formation of a LLCT state. This would result in a net increase in electron density at Re, thereby increasing backbonding to the CO ligands, inducing a lowering in the CO stretching frequencies compared to the ground state. However, the CO peak structure indicates that the state formed features high symmetry with respect to the three facial CO ligands, which is apparent from the narrowness of $\nu_{ss}(\text{CO})$ and an absence of splitting among the two $\nu_{as}(\text{CO})$ modes. Notice that formation of the (L$\rightarrow$bpy) LLCT state would result in very different charges on the bpy and L ligands and lowering of the symmetry of the environment for the three CO groups. Thus, the data suggest that the final state formed in Re3DMABN is not LLCT in character. The observed spectral changes are consistent with evolution of the MLCT state to a ligand localized (IL) triplet excited state. In addition, for 4DMABN in hexane, the CN frequency in the triplet state is found to be 175 cm$^{-1}$ below that in the ground state;\textsuperscript{126} although no data are available for 3DMABN, formation of a strongly polarized (amine $\rightarrow$ CN) triplet state seems plausible. Thus, the excited state that
decays to the ground state with a lifetime of 23 µs is assigned to a 3DMABN localized triplet state.

To clarify that the long-lived state is indeed a localized triplet state, we studied its quenching by pyrene, an aromatic hydrocarbon with a low-energy triplet state and a characteristic triplet visible absorption spectrum. Pyrene is found to be an effective quencher of the long lived excited state of Re3DMABN with the second-order quenching rate constant of 4.9 x 10^9 M^{-1}s^{-1}. The transient absorption spectral changes observed in the quenching experiment, illustrate disappearance of the absorbance of Re3DMABN and appearance of the characteristic pyrene triplet absorption transitions at 415 and 520 nm. This result supports the assignment of the thermally equilibrated excited state of Re3DMABN in DCM as a triplet state localized on the 3DMABN ligand.

The change in the CN bond order in the IL triplet state can be evaluated from the CN frequency shift. The CN mode shift of 128 cm^{-1} corresponds to a relative change in the υ(CN) force constant with k_{GS}/k_{ES} ~ 1.12. Notice that the ratio of nitrile to imine (triplet bond to double bond) force constants is approximately 1.8. Thus, the magnitude of the frequency shift in the IL triplet state represents a relatively small decrease in the CN bond order. The TRIR spectra of this complex very clearly illustrate complete conversion of the initially formed \(^3\)MLCT state into a strongly polarized state localized on the 3DMABN ligand.

**Re3DMABN in MeOH/DCM: Equilibrium of MLLCT and \(^3\)IL States.** The excited state prepared at 200 fs after Re3DMABN excitation in the mixed solvent is very similar to that in DCM, as indicated by a similarity of the frequency shifts of the CO and CN modes (Figure 4.7B). The υ(Ph) frequency is shifted to lower values by ca. 5-8 cm^{-1}, showing a
ground state bleach cancellation at the low-frequency side. As in DCM, these spectral features are assigned to the formation of the Re→bpy MLCT state.

The spectral changes observed in the picosecond dynamics of the Re3DMABN excited state differ dramatically from those in pure DCM but occur with similar characteristic times of ca. 7 and 23 ps. Neither of the CO stretching modes shifts to lower frequency with time as in DCM. Instead, the CO peaks evolve further to higher frequency with a characteristic time of 6-7 ps, which is assigned to solvation and vibrational cooling processes. The \( \nu_{\text{as}}(\text{CO}) \) peak in the excited state (at \( \sim 2070 \text{ cm}^{-1} \)) shows typical vibrational Stokes-shift dynamics with a time constant of ca. 6 ps, similar to that reported by Lian and co-workers for a structurally related Re carbonyl complex.\(^{127-128}\) Surprisingly, the CN mode peak in the excited state evolves similarly to that in DCM. The initial absorption at 2244 \text{ cm}^{-1} is reduced essentially to zero with a decay time of ca. 23 ps, while a new absorption grows in concomitantly at ca. 2125 \text{ cm}^{-1}. The frequency shift in the mixed solvent (-135 \text{ cm}^{-1}) is even larger than that in DCM (-127 \text{ cm}^{-1}) indicating that the state formed is even more polar. Methanol absorption prevented measurements below 1560 \text{ cm}^{-1}, so the frequency of the \( \nu(\text{Ph}) \) mode in the relaxed state(s) could not be determined.

Thus, the dominant relaxed excited state for Re3DMABN in the mixed solvent at delays larger than 50 ps has less electron density at the Re than in the ground state (CO frequency upshift), asymmetric facial environment for the CO groups (splitting of the two \( \nu_{\text{as}}(\text{CO}) \) modes), and strong polarization of the 3DMABN ligand (large down shift of the \( \nu(\text{CN}) \)). Because both bpy and L ligands are strongly affected in this state, we refer to it as an MLLCT state, although the degree of charge shift between the ligands remains unclear. The local L triplet state is also clearly seen in Re3DMABN in MeOH/DCM: a sharp peak
at 2035 cm$^{-1}$, $v_{ss}(CO)$, and a broader peak at ca. 1915 cm$^{-1}$, $v_{ad}(CO)$, are growing in with a time constant of ca. 24 ps, although the amplitudes of these spectral features are small. The similarity of the rising time with the characteristic time of the main MLLCT state formation indicates that the two states are in equilibrium. Using the amplitude of the peak at 2035 cm$^{-1}$ in comparison to the bleach $v_{ss}(CO)$ peak and using the bleach-to-peak ratio in DCM as a reference, the contribution of the local triplet state in MeOH/DCM mixture is estimated to be ca. 15%, which places the local triplet state ca. 400 cm$^{-1}$ higher than the main triplet MLLCT state. Thus, increasing the polarity of the medium resulted in significant lowering of the $^3$MLLCT state such that it becomes the dominant state but remains in equilibrium with the 3DMABN localized $^3IL$ state.

4.3.6. Excited State Assignments and Correlation with Relaxation Dynamics

The electronic states observed experimentally, and the rates of their interconversion, are summarized in Figure 4.8. The nature of the contributing excited states in these compounds is better understood through comparison of the experimental nanosecond and ultrafast infrared data with the computational results. In addition to comparison of the vibrational frequency shifts with respect to the ground state, we analyzed how charges on different parts of the complexes (from Mulliken population analysis) change in the excited state. The dependence of the nature of the lowest energy triplet state on the solvent polarity was investigated theoretically by introducing solvent via a polarizable continuum model (PCM). To exaggerate the polarity influence and shift of the LLCT state to lower energies, the computations were performed in a medium of increased polarity with dielectric constant of 81.
Figure 4.8. State diagrams for three complexes in different solvents with approximate transition times.

In the ReBN complex, formation of a pure $^3\text{MLCT}$ state is suggested by the experiments. DFT calculations show that the Mulliken electron density on bpy in the T1 state compared to the GS is increased by 0.26e (Table 4.5), while the charge at the BN ligand stays essentially unchanged (0.02e). The computed frequency shifts between T1 and GS are generally in agreement with the shifts found experimentally for the long-lived $^3\text{MLCT}$ state: in DCM both asymmetric CO frequencies shift to higher values by 42 and 15 cm$^{-1}$, while $\nu$(CN) shifted down by -9 cm$^{-1}$. In calculations of all three complexes, the symmetric CO stretching mode is shifted to lower frequencies, demonstrating imperfections in the computations; we will not discuss it therefore in detail. Relaxation of the MLCT state to the ground state occurs in approximately 1 $\mu$s in DCM, and is somewhat shorter in the more polar solvent mixture.

Rapid formation of a MLLCT state in Re4DMABN is suggested by the TRIR experiments in both DCM and mixed solvent. Appearance of an additional state formed with 70 ps characteristic time from the MLLCT state is found in the mixed solvent; this
state has features of a LLCT (L→bpy) state. The T1 state computed for Re4DMABN in DCM has complex electron density redistribution, with substantial electron density depletion from the dimethyl aniline (-0.42e) and electron density gain at the bpy (0.67e, Table 4.6). Based on the computed charge shifts, the MLLCT state has 64% LLCT (L→bpy) and 36% MLCT (Re→bpy) character. The computed vibrational frequency shifts match reasonably well with the experiment. For example, the v(CN) and v_{ss}(Ph) frequencies shift down by -47 and -19.5 cm\(^{-1}\), compared to the experimental shifts of -46 and -10 cm\(^{-1}\). The v_{ss}(bpy) is shifted by -57 cm\(^{-1}\), compared to -73 cm\(^{-1}\) in the experiment (peak at 1538 cm\(^{-1}\), Figure 4.6A). For isolated 4DMABN molecules in methanol, hydrogen bonded intramolecular charge transfer (HICT) structures were identified in the excited state by Kwok and coworkers.\(^{129}\) The H-bonding occurs at the cyano group and results in an additional ca. 20 cm\(^{-1}\) down-shift of the CN frequency compared to that in the intramolecular charge transfer state. Not surprisingly, no second peak was found in the excited state of Re4DMABN, likely because the CN site is shielded by coordination to the rhenium atom.

**Table 4.6.** Experimental shifts in infrared frequencies immediately following 402 nm excitation and subsequent further change in frequency to reach thermally equilibrated state.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ES1-GS -&gt; ES2-ES1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v_{as2}(CO)</td>
</tr>
<tr>
<td>Re4DMABN MeOH/DCM</td>
<td>+28⇒+4⇒-4</td>
</tr>
<tr>
<td>Re4DMABN DCM</td>
<td>+27⇒+4</td>
</tr>
<tr>
<td>Re3DMABN MeOH/DCM</td>
<td>+33⇒+3.5</td>
</tr>
<tr>
<td>Re3DMABN DCM</td>
<td>+34⇒-59</td>
</tr>
<tr>
<td>ReBN DCM</td>
<td>+30⇒+6</td>
</tr>
</tbody>
</table>
The experimental results for Re4DMABN in the mixed solvent showed two states at equilibrium, one being very similar to the MLLCT state characterized for Re4DMABN in DCM and another, denoted as LLCT, featuring substantial 4DMABN→bpy charge transfer character. To stabilize in calculations the LLCT state vs. MLLCT state, the Re4DMABN triplet excited states was computed in water described via the PCM model. The computed T1 state in water is found to have a large LLCT (4DMABN→bpy) contribution of ca. 81%. One asymmetric CO mode is shifted to lower frequency by -5 cm\(^{-1}\) with respect to their mean frequency in the GS (in agreement with the experimental peak at ca. 1910 cm\(^{-1}\)), while another is shifted to higher frequencies by 19 cm\(^{-1}\). The CN frequency is shifted down by -41 cm\(^{-1}\), which is very similar to that in the MLLCT state found in DCM (-47 cm\(^{-1}\)). These results suggest that the intensity decrease of the peak at 2190 cm\(^{-1}\) (Figure 4.6B) occurs due to reduction of the IR intensity of \(\nu(\text{CN})\) in the LLCT state and explains why no separate absorption peak was observed for the LLCT state. The computed shift of the \(\nu_{ss}(\text{Ph})\) frequency is -28 cm\(^{-1}\), compared to the experimental shift of -47 cm\(^{-1}\). Importantly, the \(\nu_{ss}(\text{Ph})\) absorption peak in the LLCT state does not overlap with that in the MLLCT state, providing a convenient observation frequency for evaluating the relative populations of the two state. The \(\nu_{ss}(\text{Ph})\) absorption at 1593 cm\(^{-1}\) decreases by ca. 2.1 fold with the rate constant of ca. 70 ps, which places the LLCT state slightly (150 cm\(^{-1}\)) below the MLLCT state. To summarize, the excited states computed for Re4DMABN in the two solvents characterize reasonably well the experimental observations (Figure 4.8).

The characteristic time to establish equilibrium among MLLCT and LLCT states, 70 ps, could be associated with the nonradiative decay process from the higher excited states to the triplet-ground state T1. For Re4DMABN compound, the vertical excitation of
energy between T1 and T2 is about 0.2 eV and that between S2 and T2 is approximately 0.5 eV. In addition, it was found in DCM solvent that there exists another local minimum whose energy is about 0.24 eV higher than that of the equilibrium geometry of the T1 state. Charge population analysis showed that this high-energy triplet minimum is a MLCT state, and single point calculations indicated it is not on the lowest triplet state. Therefore, it may correspond to an equilibrium structure on one of the triplet surfaces. According to the perturbation theory, the small energy gap between the triplet states will result in the strong nonadiabatic interaction. Indeed, the nature of the T1 state global minimum, MLLCT, reflects this multireference nature of its electronic wave function. The relatively long equilibrizing time could be attributed to the increased life time of the higher triplet excited state, which is caused by the stabilization of the charge separation due to the polar solvent. Upon UV-excitation, the molecule is populated to the singlet MLCT state. Spin-orbit coupling will transfer the population onto the triplet manifold, and finally the system will relax to the lowest triplet ground state through the nonadiabatic transitions. In the course of this relaxation process, the CT nature changes from MLCT to MLLCT.

Transitions between different structural minima may also be responsible for the observed 70 ps time constant. The structures in the T1 states in the two solvents were compared, but no large changes were found. For example, a variation of the Re-N-C angle, anticipated due to stronger contribution of the quinoidal resonance 4DMABN structure in the polar solvent, was found to be too small (~0.26°) to support the idea that such motion is responsible for the 70 ps process.

The excited-state spectral changes observed experimentally for Re3DMABN in DCM are well described by the DFT calculations. A \(^3\)MLCT state is rapidly formed in
excited **Re3DMABN** in both DCM and in mixed solvent. In DCM a new state is formed with a 20 ps time constant, which has spectroscopic features consistent with being a local 3DMABN triplet state. The computed T1 state in DCM is predicted to be mostly a $^3I_L$ state: The overall charge on the Re center and 3DMABN ligand changes only by -0.014 and 0.093, while the change of the charge at the dimethylamino and phenyl moieties together is +0.25, where the electron density is donated mostly to the cyano group (Table 4.5). The frequencies of both CO asymmetric stretches shift to lower frequencies by -14 and -20 cm$^{-1}$, compared to a ca. -25 cm$^{-1}$ experimental shift, and the environment remains symmetric for the three facial carbonyls as the two frequencies remain close to each other with a 12 cm$^{-1}$ separation, compared to the 10 cm$^{-1}$ separation in the ground state. The CN stretching frequency is shifted by -128 cm$^{-1}$, compared to the experimental shift of -127 cm$^{-1}$. The computed shift of the $v_{sa}(\text{Ph})$ mode is -75 cm$^{-1}$, compared to observed -66 cm$^{-1}$. The overall match is good, which confirms that this excited state is mostly localized at the 3DMABN ligand. The T1 calculations of 3DMABN in water show very little differences from those in DCM. Essentially, the lowest state computed for **Re3DMABN** in water remains the $^3IL$ 3DMABN localized state, although it became slightly more polarized, which can be seen from an increase of the overall charge at the dimethylamino and phenyl moieties, which is +0.26, and from a larger CN frequency shift of -134 cm$^{-1}$. The experimentally observed MLLCT state is not computed as the lowest energy triplet state. The origin of the discrepancy is currently unclear.$^{130}$

Assignment of excited states was reported in the literature for several Re tricarbonyl complexes. The authors indicated formation of LLCT states in some of the systems. The assignment of the LLCT state formation was often based on behavior of CO frequencies,
sometimes reinforced by lifetime measurements and/or DFT computations. For example, there are several reports where the down-shift of the CO frequencies (both asymmetric and symmetric) with the respect to the GS is associated with formation of the LLCT state.\textsuperscript{110, 131} Our results indicate that the downshift of the CO frequencies alone does not necessarily indicate formation of the LLCT state in Re complexes. For example, all our data on Re3DMABN in DCM, which include TRIR data for many vibrational modes, excited state lifetime measurements, triplet state quenching experiments, and DFT calculations, unequivocally indicate that a \textsuperscript{3}ILCT triplet state is formed, although all CO frequencies in this state shift to lower values. Certainly, the inclusion of a variety of vibrational labels in TRIR measurements implemented in this study increases greatly the confidence level of the assignment. For example, the CO frequency changes in the excited state of Re4DMABN in the mixed solvent are not conclusive of the LLCT state formation without considering \( \nu(CN) \) and \( \nu_{ss}(\text{Ph}) \) peak behaviors; the \( \nu_{ss}(\text{Ph}) \) peak down shift by ca. 65 cm\textsuperscript{-1}, supported by DFT calculations, clearly indicates formation of the state with dominant LLCT character.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure49.png}
\caption{A three-state model describing charge-transfer extent in Re4DMABN and Re3DMABN in the two solvent systems.}
\end{figure}
Quinoidal Resonance Structures of 4DMABN Lower the Charge-Transfer Extent in Re4DMABN Compared to Re3DMABN. The difference between the excited states of Re3DMABN and Re4DMABN can be related to ability of the two DMABN ligands to form quinoidal charge-transfer resonance structures associated with partial or full charge transfer from the dimethylamino moiety to the nitrile moiety (Figure 4.10). Quinoidal charge transfer resonance structure is very favorable (has low energy) in 4DMABN but is unfavorable in 3DMABN because of the 1,3 substitution pattern. As a result, the 4DMABN ligand will likely behave as a single entity in all charge-shift reactions, so that the changes are delocalized over the whole ligand. In contrast, when the 3DMABN ligand is involved in electron donation the electron density will mostly be drawn from its amino moiety. Figure 4.9 presents a qualitative three-state state coupling diagram for Re4DMABN and Re3DMABN compounds in DCM and in a polar solvent. These states include a pure MLCT (Re→bpy) state characterized by an electron density shift from Re to bpy of ca. 0.2e (as in ReBN, Table 4.5), a formal full-electron CT (L→bpy) state, and an ideal fully L-localized triplet state, 3IL. Proper mixing of these three states results in preparation of the characteristic states of the complex. The ideal MLCT and CT states are both associated with an increase of electron density on the bpy and therefore couple strongly. The coupling of the 3IL state to the two other is assumed in comparison. Weak coupling of the 3IL state to the MLCT and CT states is in agreement with experimental observations that the two states (MLLCT and 3IL) are in equilibrium for Re3DMABN in MeOH/DCM (Figure 4.8). The MLCT and CT states are strongly coupled in Re4DMABN (large spatial overlap of the involved wavefunctions), enabled by the quinoidal resonance forms (Figure 4.10). In contrast, coupling in Re3DMABN is much weaker because of the
larger distance for charge transfer (from amine to bpy) and the absence of bridge polarization because of the meta-conjugation pattern. In the model of Figure 4.9, the CT states of both compounds in DCM are placed substantially above the MLCT state in energy, as motivated by the experimental data. The ideal \(^3\)IL state is placed lower than the CT state just below the ideal MLCT state for both compounds in DCM. In polar solvent, the CT state shifts to substantially lower energies for both Re\(^4\)DMABN and Re\(^3\)DMABN, while the \(^3\)IL state is affected little by the solvent polarity. Strong MLCT/CT coupling for Re\(^4\)DMABN results in small shifts of the coupled states in DCM, because their initial energy gap is larger than the strength of the coupling.\(^{132}\) The resulting low-energy state in DCM, labeled as MLLCT, has a dominant contribution of the MLCT state: the CT state contribution, evaluated as the loss of the charge density by the 4DMABN ligand is ca. 42\% (Table 4.5). As confirmed experimentally, this state is the lowest energy excited state in Re\(^4\)DMABN in DCM. In the polar solvent, the ideal CT state is shifted below the ideal MLCT state, which results in much larger CT character of the state formed upon their mixing (60\%, denoted as LLCT). Although the ideal CT state is now lower than the ideal MLCT, their strong coupling still results in formation of a mixed state with only partial CT character. An extremely large down shift is required to decouple the two states and obtain essentially a pure CT state in the complex; it is unlikely that any solvent is capable of shifting the ideal CT state in Re\(^4\)DMABN that low. A similar situation is found for Re\(^3\)DMABN, with the main difference in the coupling strength of the ideal MLCT and CT states. Weaker coupling and off-resonant conditions result in only a small down shift of the mixed MLCT/CT state in DCM, which places it higher than the \(^3\)IL state. In a polar solvent, the ideal CT state is in close resonance with the ideal MLCT state, resulting in a
larger down shift of the mixed state, labeled as MLLCT, which is now very close to the \( ^3{\text{IL}} \) state; equilibrium between the two states is observed in the MeOH/DCM solvent (Figure 4.8). Based on the experimental observations, the lowest energy excited state in \textbf{Re3DMABN} in MeOH/DCM is denoted as MLLCT; it seems possible to drive this state lower and prepare a pure CT state if the polarity of the solvent is further increased or the CT state energy is lowered by structural alterations in the complex. Similar efforts with 4DMABN will give only partial success due to a strong MLCT/CT coupling. Satisfyingly, this three-state model describes well the majority of the experimental and computational observations.

![Resonant structures of 4DMABN, neutral (A and B) and cationic (C and D). Structure A is dominant for the ground state, while the quinoidal structure D contributes significantly for the 4DMABN cation. Panels E and F show resonant structures (neutral and cationic) for 3DMABN.](image)

\textbf{Figure 4.10.} Resonant structures of 4DMABN, neutral (A and B) and cationic (C and D). Structure A is dominant for the ground state, while the quinoidal structure D contributes significantly for the 4DMABN cation. Panels E and F show resonant structures (neutral and cationic) for 3DMABN.

\section*{4.4. Conclusions}

Excited state properties of a series of Re\(^1\)(bpy)(CO)\(_3\)L compounds were studied using time-resolved vibrational and electronic spectroscopy methods and DFT computations. The \textbf{Re4DMABN} and \textbf{Re3DMABN} complexes exhibit strongly solvent-dependent luminescence, having strong emission in dichloromethane (DCM) with microsecond lifetimes, but being nearly completely quenched in the mixed MeOH/DCM
solvent. Despite similarities in redox properties for **Re4DMABN** and **Re3DMABN** and in the excited state lifetimes in each solvent, the nature of the states observed in these systems is very different. For the **Re4DMABN** complex in DCM, essentially instantaneous formation of a long-lived (0.8 μs) triplet MLLCT excited state is found, while formation of the LLCT (4DMABN→bpy) state in close proximity to the MLLCT state is observed in the MeOH/DCM mixed solvent. The presence of this state, confirmed by DFT calculations is believed to be responsible for drastic shortening the excited-state lifetime to less than 10 ns in the mixed solvent. An essentially pure MLCT excited state is formed within 0.2 ps of excitation of **Re3DMABN** in both solvent systems, although its dynamics are solvent dependent. In contrast to **Re4DMABN**, a long-lived (23 μs) intraligand triplet ($^3$IL, $^3$(π-π*)) state is formed in **Re3DMABN** in DCM, while, in the mixed solvent, an equilibrium is observed between $^3$IL and MLLCT states for **Re3DMABN**. The presence of the MLLCT state accounts for the excited-state lifetime shortening by three orders of magnitude for **Re3DMABN** in the mixed solvent (20 ns). The set of excited states in these compounds appeared to be complex enough that their detailed characterization requires use of a combination of experimental methods, such as ps-ns TRIR, excited-state lifetime, and triplet state quenching measurements, as well as DFT computations. In addition, incorporation of multiple IR labels on different ligands in TRIR measurements is shown to be crucial in assessing the nature of the electronic states associated with charge localization, polarization, and transfer. A simple three-state model is proposed that describes well the origin of the drastic differences in the excited states involved in these two compounds. The model predicts that, even in a very polar solvent, the lowest energy state in **Re4DMABN** will not be a pure CT state. On the contrary, for **Re3DMABN** it seems possible to generate
an essentially pure CT state if the polarity of the solvent is increased or the CT state energy is lowered by structural alterations in the complex.

4.5. Acknowledgment.

Support by the National Science Foundation (CHE-1012371) is gratefully acknowledged. Tod Grusenmeyer performed the synthesis of the Re compounds and ns transient absorption and fluorescence measurements. Zheng Ma and Peng Zhang performed the ground state and excited state DFT calculations and charge analysis for the Re complexes.
Chapter 5. Full-Electron Ligand-to-Ligand Charge Transfer in a Compact Re(I) Complex

The work presented in this chapter has been published in the following paper:


5.1. Overview

The control and manipulation of photoinduced intramolecular charge transfer is of central importance for developing photosensitizers, optical limiters, sensors, and other photonic devices. Donor-bridge-acceptor compounds have been explored for three decades to characterize the structural and dynamical factors that control photoinduced charge separation and recombination (see refs.\(^{133-135}\)). Recent interest has focused, as well, on using IR excitation to control charge transfer in small molecules.\(^{47, 97, 136}\)

Transition metal complexes provide a robust scaffold to investigate charge transfer. Complexes of substitutionally inert metals are amenable to modifications and are attractive for performing photoinduced electron-hole separation. Indeed, the characteristic UV-vis absorption spectra of transition metal complexes are often derived from metal to ligand and ligand to metal charge-transfer transitions (MLCT and LMCT). The distance of the charge shift in MLCT and LMCT states is typically small, and the extent of charge transfer corresponds to less than one electron. Enhancing the oscillator strength for such transitions indeed tends to produce complexes with strongly coupled spatially extended states.
Nevertheless, MLCT states can produce charge polarized exited states; further polarization can be achieved by forming ligand-to-ligand charge-transfer states (LLCT) where a complete charge separation can be obtained. Here, we show that, by tailoring the properties of two redox active ligands, a LLCT state with essentially full charge separation can be obtained while keeping the compound compact. The electronic decoupling of the metal center and a ligand is accomplished not by increasing the distance between the redox active centers but by manipulating the electronic coupling interactions and energy matching of the component parts of the complex (metal and ligands).

The specific systems studied are rhenium tricarbonyl diimine complexes, [Re\(^{(L)}\)(CO)\(_3\)(N,N)(L)], with luminescent MLCT excited states that have lifetimes of hundreds of nanoseconds. Excitation into the singlet MLCT state is followed by relaxation into the triplet MLCT manifold within a few hundred femtoseconds. Note that the fast intersystem crossing occurs due to a strong spin-orbit coupling at the Re metal center; as a result, most states accessed experimentally in this work have a triplet character, which is not indicated explicitly in the notation. A useful handle for observing evolution of the MLCT state is provided by the strong CO stretching modes of these complexes. These CO modes were shown to have high sensitivity to redistribution of electron density in the excited state, since the CO stretching modes are affected by changes in backbonding from the metal center. It is also possible to design derivatives that have functional groups with strong infrared absorption on N,N and/or L that further enhance the ability to track electron density changes during excited-state evolution.

The decay of the initially formed MLCT state and the ability ultimately to form a LLCT state is largely directed by the nature of L. In some instances, L is an easily reduced
species that results in redistribution of electron density from the N,N ligand to L in the excited state. Examples also exist where L is a strong electron donating ligand, and formation of an L to N,N ligand to ligand charge transfer (LLCT) state occurs. The rate of the charge migration in these systems can vary from sub-ps to ns time scales and is often strongly solvent dependent.

These latter systems, in which ligand to ligand electron transfer occurs ostensibly to form a fully charge-separated state, has been the subject of numerous studies of photoinduced intramolecular electron transfer (for reviews see ref.133-135). A key approach to evaluating electron transfer in systems consisting of an electron donor, a chromophore and an electron acceptor, has been to observe quenching of the luminescence of the chromophore concomitant with transient spectral signatures of the oxidized donor and reduced acceptor. We have recently examined [Re\(^{(1)}\)(CO)\(_3\)(N,N,L)] compounds with a sufficiently low L oxidation potential to exhibit LLCT (L→bpy) transitions, where L is 3-dimethylaminobenzonitrile (3DMABN) or 4-dimethylaminobenzonitrile (4DMABN). The characteristic quenching of the MLCT luminescence is observed, supporting the assignment of intramolecular electron transfer from the DMABN ligand to the N,N ligand. However, TRIR studies clearly show that coupling between these ligands and the metal center strongly influences the degree of charge transfer. This coupling is especially strong in [Re(bpy)(CO)\(_3\)(4DMABN)]\(^+\) (Re4DMABN), where a quinoidal resonance structure of the 4DMABN ligand facilitates the interaction. Substantial suppression of the Re-L interaction was achieved by changing the position of the amino group on the phenyl ring from 4 to 3 in [Re(bpy)(CO)\(_3\)(3DMABN)]\(^+\) (Re3DMABN). The reduced coupling, however, results in a higher energy of the coupled state and an intra-ligand triplet (\(^3\)IL).
localized on 3DMABN is found to be the lowest energy excited state. In order to achieve a LLCT state exhibiting full electron transfer, its energy needs to be lowered relative to the \(^3\)IL state of the 3DMABN, while maintaining LLCT state decoupling from the MLCT state(s) of the complex.

Here we describe a study of Re(I) tricarbonyl compounds that feature a bpy ligand functionalized with a two ester groups (DCEB) (Scheme 5.1) that serves as an electron accepting ligand. The electron donating ligand (L) is 3DMABN, which supports state decoupling.\(^{21}\) In addition to the compound with expected charge separation, \([\text{Re(DCEB)(CO)}_3(3\text{DMABN})]^+\) (ReEBA), its photoredox inactive analog, \([\text{Re(DCEB)(CO)}_3(\text{PhCN})]^+\) (ReEB, \text{PhCN} = benzonitrile), was also studied. The measurements were performed in solvents of different polarities using fs/ps TRIR and nanosecond transient absorption. Vibrational labels placed on different positions of the complex were used to monitor excited state kinetics. Excited states assignments were made using a combination of experimental data and the results of DFT computations.

\[\text{ReEBA} \quad \text{ReEB} \quad \text{Re3DMABN}\]

\textbf{Scheme 5.1.} Structures of ReEBA, ReEB, and Re3DMABN.
5.2. Experimental Details

The detailed description of the time-resolved 3-pulse spectrometer is presented in Chapter 3.4. Cyclic voltammetry techniques used in this chapter is described in Chapter 4.2.3. The nanosecond spectroscopy techniques used in this chapter is described in Chapter 4.2.2.

Detailed quantum chemistry method is presented in Chapter 3.8.

5.3. Results

5.3.1. Electrochemistry

The redox properties of ReEB and ReEBA illustrate the significant differences among these complexes and the previously studied Re3DMABN associated with changing the diimine ligand from bpy to DCEB (Table 5.1). The carboxyethyl substituents on the bpy ligand in DCEB lower the first one electron reduction potential by 0.34 and 0.39 V in DCM and CH₃CN, respectively relative to the bpy complex. The potential of the first oxidation, reflecting the 3DMABN⁺/3DMABN reduction, is altered only slightly upon changing the diimine ligand from bpy to DCEB. As was demonstrated elsewhere,¹⁴⁴ the diimine reduction potential decrease translates directly into a lowering of the MLCT state energy, as reflected in the luminescence maxima in both polar and nonpolar solvents.

Table 5.1. Redox potentials of ReEBA and Re3DMABN in DCM and CH₃CN vs. Ag/AgCl.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( E^0(2+/+) ), (( \Delta E_p ), V) in DCM</th>
<th>( E^0(2+/+) ), (( \Delta E_p ), V) in CH₃CN</th>
<th>( E^0(+/0) ), (( \Delta E_p ), V) in DCM</th>
<th>( E^0(+/0) ), (( \Delta E_p ), V) in CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re3DMABN</td>
<td>1.28 (0.24)</td>
<td>1.17 (0.14)</td>
<td>-1.13</td>
<td>-1.17 (0.08)</td>
</tr>
<tr>
<td>ReEBA</td>
<td>1.15 (0.18)</td>
<td>1.17 (0.12)</td>
<td>-0.79</td>
<td>-0.78 (0.07)</td>
</tr>
</tbody>
</table>
5.3.2. UV-Vis Linear Absorption and Luminescence Spectra

The absorption maximum at 335 nm for ReEBA in both DCM and NM is assigned to the DCEB ligand-localized $\pi$-$\pi^*$ transitions (Figure 5.1). The presence of the ester groups on the DCEB ligand causes this transition to be red shifted compared to the bpy-localized $\pi$-$\pi^*$ transitions in Re3DMABN (320 nm). The broad spectral features of ReEBA from 360 nm to 460 nm include a 3DMABN ligand-localized transition ($\lambda_{\text{max}} = 370$ nm) and an MLCT state absorption as a weaker absorption that tails up to 460 nm. Solvent polarity affects the strength of the transitions, but does not induce major changes in their nature.

**Figure 5.1.** UV-Vis absorption spectra of ReEBA in DCM and NM measured at 9 mM concentration in the sample cell with 50 μm path length. Green bars show the calculated UV-Vis absorption transitions using TD-DFT at Franck-Condon geometry.

The complexes exhibit luminescence in nonpolar solvents at room temperature. Emission spectral maxima, quantum yields, lifetimes and decay rate constants are given in Table 5.2. Luminescence from the DCEB complexes (ReEBA and ReEB) is approximately 1100 cm$^{-1}$ lower in energy than in the corresponding bpy complex (Re3DMABN), increasing the likelihood that the MLCT state is lower in energy than the $^3\text{IL}$ state of the
3DMABN ligand (the observed excited state of Re3DMABN in DCM) in these complexes.

The emission yield of ReEB is ca. 30 percent in DCM at room temperature, but the dimethylamino derivative ReEBA is only very weakly luminescent ($\Phi_{\text{lum}} = 0.003$), indicating a nonradiative process involving a dark state. Luminescence of the ReEB and ReEBA exhibit a significant red shift ($800 - 1000 \text{ cm}^{-1}$) upon changing the solvent from DCM to mixed DCM/NM, illustrating that the MLCT state is stabilized in more polar solvents. The luminescence yield of the ReEBA complex becomes even weaker in the more polar solvent, suggesting that the energies of both the emitting and the dark state decrease with increasing solvent polarity.

**Table 5.2.** Luminescence maximum ($\lambda_{\text{max}}$) and quantum yield ($QY_{\text{lum.}}$) and the excited state lifetimes measured via luminescence ($T_{\text{lum.}}$) and transient absorption ($T_1$) for the complexes in aerated solvents at room temperature. The radiative ($k_r$) and nonradiative ($k_{\text{nr}}$) relaxation constants are also shown.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Re3DMABN</th>
<th>ReEB</th>
<th>ReEBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>DCM</td>
<td>DCM/MeOH</td>
<td>DCM</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}, \text{nm}$</td>
<td>528</td>
<td>565</td>
<td>566</td>
</tr>
<tr>
<td>$QY_{\text{lum.}}$</td>
<td>0.003</td>
<td>$&lt; 0.001$</td>
<td>0.26</td>
</tr>
<tr>
<td>$T_{\text{lum.}}, \mu s$</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>0.94 ± 0.02</td>
</tr>
<tr>
<td>$T_1, \mu s$ ($\lambda, \text{nm}$)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23.3 ± 1.0 \text{ (450)}</td>
<td>0.02 ± 0.005 \text{ (450)}</td>
<td>0.91 ± 0.02 \text{ (350)}</td>
</tr>
<tr>
<td>$k_r, s^{-1}$</td>
<td>130</td>
<td>-</td>
<td>2.8 x 10$^5$</td>
</tr>
<tr>
<td>$k_{\text{nr}}, s^{-1}$</td>
<td>5.0 x 10$^4$</td>
<td>8 x 10$^5$</td>
<td>2.1 x 10$^6$</td>
</tr>
</tbody>
</table>

<sup>a</sup> the mean value of two components is shown;
<sup>b</sup> the lifetime measured by transient absorption at indicated wavelengths;
<sup>c</sup> 1:1 (v/v) mixture of DCM and NM was used.
<sup>d</sup> A second emission component is observed with a lifetime of ~ 800 ns; this is believed to be due to an impurity Re complex.
5.3.3. Vibrational Linear Absorption Spectra

The vibrational spectrum of ReEBA (Figure 5.2) has several readily identifiable characteristic features (Table 5.3). The weak peak at ca. 2260 cm\(^{-1}\) is the C≡N stretching mode. The peaks at ca. 2043 cm\(^{-1}\) and 1946 cm\(^{-1}\) belong, respectively, to the symmetric and two overlapping asymmetric stretching modes of the three facial carbonyl ligands. Another peak of interest at ca. 1735 cm\(^{-1}\) belongs to two C=O stretching modes of the ester groups. No signature of splitting is found, suggesting that the coupling of the two carbonyl transitions is weak. Indeed, the closest possible distance between the two C=O transition dipoles is as large as 6.2 Å; moreover, for a such conformation, the angle between the transition dipoles is close to the magic angle, which results in a minimal splitting of the two coupled state energies. As assigned previously,\(^{21}\) the ring stretching modes of the bpy, \(\nu_{ss}(bpy)\), and of the phenyl ring of 3DMABN, \(\nu_{ss}(ph)\), are also resolved in the spectra at 1610 and 1600 cm\(^{-1}\), respectively. While well resolved in the DCM solvent, in NM they overlap with a strong solvent absorption around 1600 cm\(^{-1}\). All of these modes were used in transient infrared measurements as reporters of the changes in the electron-density distribution in the compounds.
**Figure 5.2.** Linear FTIR absorption spectra of ReEBA in DCM and NM measured at 9 mM concentration in the sample cell with 50 μm path length.

**Table 5.3.** Experimental and DFT computed ground-state vibrational frequencies (in cm\(^{-1}\)) of several characteristic modes for ReEBA in both DCM and NM.

<table>
<thead>
<tr>
<th></th>
<th>ReEBA in DCM</th>
<th>ReEBA in NM</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exper.</td>
<td>DFT, GS</td>
<td>Exper.</td>
<td>DFT, GS</td>
</tr>
<tr>
<td>2258</td>
<td>2341</td>
<td>2266</td>
<td>2343</td>
</tr>
<tr>
<td>2046</td>
<td>2106</td>
<td>2043</td>
<td>2104</td>
</tr>
<tr>
<td>1949</td>
<td>2009, 2003</td>
<td>1945</td>
<td>2007, 2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1735</td>
<td>1789</td>
<td>1734</td>
<td>1786</td>
</tr>
<tr>
<td>1610</td>
<td>1612/1604</td>
<td>N/A</td>
<td>1613/1605</td>
</tr>
<tr>
<td>1600</td>
<td>1646</td>
<td>N/A</td>
<td>1646</td>
</tr>
</tbody>
</table>

**5.3.4. Transient Infrared Spectroscopy**

TRIR spectra were measured from 1600 cm\(^{-1}\) to 2300 cm\(^{-1}\) to cover the spectral region of the C\equiv N (2120 cm\(^{-1}\) to 2300 cm\(^{-1}\)), C\equiv O (1800 cm\(^{-1}\) to 2120 cm\(^{-1}\)), C=O (1640 cm\(^{-1}\) to 1800 cm\(^{-1}\)) and ring (1480 cm\(^{-1}\) to 1620 cm\(^{-1}\)) modes (Figure 5.3). The transient spectra represent the difference between the vibrational spectra in the excited and ground electronic states; positive peaks occur due to absorption of modes in the excited states and negative peaks are due to bleaching of the modes in the ground electronic state. Each vibrational mode indicated above is localized on a specific moiety (ligand) of the complex and therefore reports on changes in electron density at the respective moiety; DFT calculations on the complexes, including solvent polarization effects, support the idea of
mode localization. Analysis of all of the available spectral features is essential for a consistent assignment of the excited states character.

**Figure 5.3.** Transient infrared spectrum of ReEBA in DCM following 402 nm excitation at selected time delays. Insets show kinetics measured at indicated frequencies and their fits to single or double exponential functions.

**MLCT state formation.** All ReEBA characteristic mode frequencies change upon 402 nm excitation. The initial spectral changes, assigned to formation of the Re to bpy MLCT state, are essentially instantaneous within the time resolution of ca. 200 fs. The ν(C≡N) peak decreases in frequency by 15 cm<sup>-1</sup> and its transition dipole increases by more than a factor of 10 in the excited state (Figure 5.3). The shift and intensity increase are similar to those observed in the Re3DMABN and Re4DMABN compounds<sup>21</sup> also assigned to formation of an MLCT (Re → bpy) state.

The C≡O stretching modes are known to be useful probes of changes to the metal center charge because the π backbonding from the metal to the C≡O is strongly influenced
by the metal’s charge. An increase in the positive charge on Re will cause an upshift in the \( \nu(\text{C} \equiv \text{O}) \) frequencies. The frequency upshift values, 74 (as1), 42 (as2), and 28 cm\(^{-1}\) (ss), are larger than those for Re3DMABN in DCM in its MLCT state, which are 70 (as1), 30 (as2), and 17 cm\(^{-1}\) (ss). This indicates that the MLCT state formed features more positive charge on Re. The two \( \nu_{\text{as}}(\text{C} \equiv \text{O}) \) modes that overlap in the ground state are resolved in the excited state (Table 5.4), indicating a decreased symmetry among the environment for the three carbonyl ligands. Note that the reduction of electron density at the metal causes an upshift in the C=O frequencies but a downshift in the C≡N frequency. This is because the antibonding orbitals of the nitrile group have much higher energies than those in the carbonyls, preventing their population through the metal center.

The C=O modes of the ester groups are expected to be good reporters of the DCEB ligand charge changes. The C=O modes in the MLCT state absorb at ca. 1694 cm\(^{-1}\), which is ca. 39 cm\(^{-1}\) lower than their ground state frequency. The \( \nu(\text{C}=\text{O}) \) peak in the excited state is much broader and has a higher IR intensity than that in the ground state, which suggests that the DCEB ligand is more highly charged in the excited state. The broader spectrum may be a result of a larger splitting of the two carbonyl transitions that bear a larger IR intensity in the excited state.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \Delta_1 )</th>
<th>( \Delta_2 )</th>
<th>( \Delta_1 )</th>
<th>( \Delta_2 )</th>
<th>( \Delta_1 )</th>
<th>( \Delta_2 )</th>
<th>( \Delta_1 )</th>
<th>( \Delta_2 )</th>
</tr>
</thead>
</table>

**Table 5.4.** Experimental frequency shifts (in cm\(^{-1}\)) for indicated vibrational modes of ReEBA and Re3DMABN in the \(^3\)MLCT state vs. the ground state (\( \Delta_1 \)) and in the long-lived excited state\(^a\) vs. the ground state (\( \Delta_2 \)).
Two ring stretching modes, \( \nu(\text{bpy}) \) and \( \nu(\text{ph}) \), also undergo changes in the excited state, most notably by the appearance of a broad peak at 1540 cm\(^{-1}\). Because of the closeness of the \( \nu(\text{bpy}) \) and \( \nu(\text{ph}) \) peaks in the ground state, this excited state peak can originate from either of the two modes. The DFT calculations of the triplet excited state showed two vibrational modes with high IR intensity in this region, and both of them belong to the ring stretching modes of the bpy moiety. The two \( \nu(\text{bpy}) \) modes, which feature -38 and -61 cm\(^{-1}\) downshifts with respect to the ground state, appear as a broad peak at 1540 cm\(^{-1}\). Such a large downshift is caused by electron transfer from Re to the DCEB ligand in the MLCT state. This peak at 1540 cm\(^{-1}\) undergoes narrowing and intensity growth with a characteristic time of ca. 5.5 ps, which is typical for solvation process in DCM. Similar to that reported previously for Re3DMABN,\(^{21}\) the \( \nu(\text{ph}) \) peak at 1600 cm\(^{-1}\) is shifted by ca. 3-5 cm\(^{-1}\) to smaller frequencies, as indicated by canceled bleaching at ca. 1593 cm\(^{-1}\) in the 1-7 ps-delay spectra.

**MLCT state decay and formation of an LLCT state.** The transient IR spectra of ReEBA show large changes with a characteristic time of ca. 10 ps, which do not lead to recovery of the ground state bleach features, thus indicating formation of a new excited state. Because the state formed for ReEBA in DCM with the 10 ps time constant is long-
lived (no decay in the 3 ns time window, see Fig 3 insets) its experimental features are compared to the features of the lowest-energy triplet state, computed using the variational approach (Table 5.5).

The cyano group absorption decays to a weak and broad feature, but not to zero, indicating a large reduction in the IR intensity. DFT calculations indicate that \( \nu(C=\text{N}) \) of the lowest energy triplet state is ca. 3-fold weaker than that in the ground state (Table 5.5), while its frequency is ca. 13 cm\(^{-1}\) higher than that in the ground state. The DFT calculations indicate that the lowest energy triplet state has LLCT character.

| Table 5.5. Experimental and calculated frequency differences between the ground state and lowest energy excited state. |
|---|---|---|---|---|---|
| Solvent | \( \nu_{\text{as2}}(\text{C}=\text{O}) \) | \( \nu_{\text{as1}}(\text{C}=\text{O}) \) | \( \nu_{\text{asd}}(\text{C}=\text{O}) \) | \( \nu(\text{C}=\text{N}) \) | \( \nu(\text{C}=\text{O}) \) | \( \nu(\text{bpy}) \) |
| ReEBA DCM | Exper | -21 | -39 | -24 | N/A | -39 | -60 |
| | Cal | -10 | -22 | -24 | +13* | -31 | -36/-60 |
| ReEBA NM | Exper | -28 | -35 | -23 | N/A | -38 | N/A |
| | Cal | -21 | -28 | -23 | +15* | -34 | -40/-63 |

* DFT computed IR intensity in the excited state is more than 3 times weaker than that in the ground state.

The \( \text{C}=\text{O} \) peaks in the MLCT state found at ca. 1990 and 2070 cm\(^{-1}\) decay to the baseline with a characteristic time of 10 ps, indicating a complete depletion of the MLCT state. Concomitant with the decay, the \( \text{C}=\text{O} \) peaks at ca. 1908, 1926 and 2022 cm\(^{-1}\) grow in. The \( \text{C}=\text{O} \) frequencies in this state appear lower than those in the ground state by 39, 21 and 24 cm\(^{-1}\), which match well the computed shifts for the lowest excited triplet state (34, 22, and 28 cm\(^{-1}\), Table 5.5). Large shifts to smaller frequencies for all three \( \nu(\text{C}=\text{O}) \) modes suggest accumulation of an additional negative charge at the Re center. Such charge
redistribution is expected if an electron is transferred from the amino group of 3DMABN to Re and the DCEB ligand.

The C=O absorption peak in the MLCT state at 1695 cm\(^{-1}\) does not show much frequency shift with time, but its amplitude increases by about 12% with a 10 ps time constant. This suggests that the charge on the DCEB ligand changes little in the LLCT state compared to that in the MLCT state. The DFT computations predict a 33 cm\(^{-1}\) downshift for the C=O mode frequencies and ca. two-fold increase of their IR intensities, which reproduce the experimental observations. The excited state C=O peak does not show any decay within the probed time window of ca. 3 ns; the excited-state lifetime of 43 ns was obtained via ns transient UV-vis absorption.

The \(\nu\)(bpy) ring modes in the LLCT state show similar behavior to that of the C=O modes: the intensity growth here is accompanied by peak narrowing, which occurs with a characteristic time of ca. 5.5 ps and assigned to the solvation process in DCM and vibrational cooling.\(^{27, 121-123}\) A small 100 ps component may reflect structural rearrangements; similar components were previously observed in other Re complexes.\(^{21}\)

5.3.5. Solvent Effects.

The TRIR spectra of ReEBA measured in solvents of different polarities, i.e., less polar DCM (Figure 5.3) and more polar nitromethane (NM, Figure 5.4), were compared. Due to solvent absorption, no spectra were recorded below 1650 cm\(^{-1}\) in NM. Although the spectral features of ReEBA in NM are similar to those in DCM and a similar MLCT state conversion to LLCT state was observed with a similar time constant of ca. 10 ps, several differences are noteworthy. First, the lifetime of the LLCT state in NM (2.4 ns) is much shorter than that in DCM (43 ns). In addition, compared to that in DCM, there are larger
upshifts of the three C≡O peaks in the MLCT state in NM and the absence of an additional rise with time in the C≡O absorption in NM at ca. 1690 cm\(^{-1}\) following initial MLCT state formation. These observations point to the same effect, namely that a larger positive charge is formed at Re in the MLCT state in NM, and a larger negative charge is formed at DCEB upon MLCT state formation. Similar C≡O peak dependences were observed for Re3DMABN and Re4DMABN compounds when switching the solvent from DCM to DCM/MeOH mixture.\(^{21}\)

**Figure 5.4.** Transient infrared spectrum of ReEBA in NM following 402 nm excitation at selected time delays. Insets show kinetics measured at indicated frequencies and their fits to a single or double exponential function.

### 5.4. Discussion

The experimental and computational data described here allow us to track the changes in the electron density between the ground and excited states of the ReEBA complex. As the solvent polarity does not strongly affect the MLCT to LLCT processes, we focus on the data for ReEBA in DCM below.
Formation of the Re(dπ)→DCEB(π*) MLCT state is apparent from the TRIR data. The C≡O modes alone are sufficient to conclude that the upshift of all three C≡O mode frequencies is characteristic of establishing increased positive charge at the metal. The frequency shifts are uniformly larger than those observed previously in Re3DMABN and ReBN compounds (Table 5.4), suggesting that a larger amount of charge is transferred from the metal. Formation of the MLCT state is faster than our time resolution of ca. 200 fs due to a strong spin-orbit coupling at the Re atom. A considerable number of reports indicate that the electronic relaxation time to form a triplet MLCT state for Re complexes is a few hundred femtoseconds. Other vibrational modes in the complex also report the formation of the MLCT state. For example, the downshift of the ν(C≡N) frequency by 15 cm⁻¹ is similar to that for ReBN (-10.5 cm⁻¹) and Re3DMABN (-12 cm⁻¹). The amount of charge transferred from the metal to the ligand varies for different complexes. It is expected that the amount of charge transfer increases from Re3DMABN to ReEBA in accord with a decrease in the reduction potential for the electron accepting ligand (Table 5.1).

The lowest energy triplet excited state of ReEB is the MLCT state, which can serve to characterize the amount of charge transferred in the MLCT state for ReEBA and to correlate the charge transfer to the frequency shifts of vibrational labels in the DCEB ligand. The DFT computation of the lowest energy triplet in ReEB predicts that ca. 0.54 electron charge is transferred to the DCEB ligand in the MLCT state.

The MLCT state relaxes rapidly (10 ps) into another state that is assigned as an LLCT state. The ν(C≡O) frequency shifts indicate the formation of a negative charge on the metal compared to that in the GS, although the assignment of the state formed as LLCT is less unambiguous based on ν(C≡O) peaks alone as the 3IL state at 3DMABN is also
characterized by a downshift of the $\nu(C=O)$ frequencies.\textsuperscript{21} Combined use of all measured IR reporters provides a clear picture for the state assignment. In particular, the $\nu(C=\equiv N)$ mode is instrumental in distinguishing the LLCT and $^3$IL states, as it shifts to smaller frequencies by ca. 120 cm$^{-1}$ in the latter. Thus, a large frequency shift of $\nu(C=\equiv N)$ in the $^3$IL state results from the electron density shift from the dimethyl amino moiety and phenyl ring to the CN group.\textsuperscript{21,126} A lack of $\nu(C=\equiv N)$ peak shift to the ca. 2130 cm$^{-1}$ region indicates that electron density changes do not involve the CN group, signifying that formation of the $^3$IL state is not occurring in ReEBA. The C=O modes at 1735 cm$^{-1}$ serve as reporters of the DCEB ligand charge redistribution. After its initial downshift of 36 cm$^{-1}$ in the MLCT state, the excited state C=O modes show no further shift and only a small increase (less than 20%) in the IR intensity with a characteristic time of 10 ps following the instantaneous rise of the peak. The DFT calculations predict a 33 cm$^{-1}$ frequency downshift of $\nu(C=O)$ in the lowest energy excited state, which matches the experimental value well; this downshift corresponds to an increase in the negative charge on the DCEB ligand. Thus, with formation of the MLCT state, the DCEB moiety receives large amount of negative charge from the Re atom. The amount of negative charge at DCEB increases further with formation of the LLCT state, now the electron density is transferred from the 3DMABN ligand (Figure 5.5). The same picture is reported by the bpy ring stretching mode peak; the peak at 1539 cm$^{-1}$ is formed in the MLCT state and shows only a minor amplitude increase and narrowing with the MLCT $\rightarrow$ LLCT conversion.
Figure 5.5. Changes in Mulliken charges at different moieties of ReEBA in $^3$MLCT and LLCT states vs. the ground state. Notice that the charge changes given for the MLCT state were computed for the lowest excited triplet state for ReEB in DCM.

The combined electrochemical and luminescence data are also consistent with the relative populations of the MLCT and ILCT states described above. The energy of the long-lived excited state for ReEBA in DCM is approximately 2.2 eV, based on the luminescence maximum. The energy of the LLCT state can be approximated from the difference in the potential between the coordinated 3DMABN$^+$/3DMABN reduction and the coordinated DECB ligand, which is 1.94 V in DCM. Thus the MLCT state is about 0.25 V higher in energy than the LLCT state, and there is less than 0.1 % MLCT state present at equilibrium. The same analysis in the more polar solvent indicates that the MLCT state is approximately 0.15 V higher in energy than the LLCT state, still leaving excited less than 1 % of the MLCT state in an equilibrium of the two states. The results are consistent with the transient IR data that show complete disappearance of the MLCT state and the extremely weak luminescence observed from ReEBA in both DCM and DCM/NM. Thus, given this equilibrium model, it is reasonable to assign this luminescence as originating from an MLCT state rather than the predominant LLCT state.

The excited-state lifetime of the lowest-energy state of ReEBA in DCM solvent was obtained using nanosecond transient absorption spectroscopy. The excited-state lifetime measured for ReEBA is 43 ns, which is ca. 3 orders of magnitude smaller than that
for Re3DMABN (23 μs) in the same solvent, DCM. The large reduction in the lifetime of ReEBA also indicates that the lowest energy state differs from Re3DMABN (which is $^3$IL). A substantial solvent dependent lifetime further supports the assignment: the lifetime reduces from 43 ns in DCM to 2.4 ns in NM. The large influence of solvent polarity on the excited state relaxation process in ReEBA indicates that the excited state is strongly polarized, suggesting that it has a LLCT character. As stated above, the energy of the charge separated state is greater than 1.9 eV in both solvents and differs by only 10 mV between the two solvents. In addition, the rigidity of the participating electron donor and acceptor in ReEBA suggests that the inner sphere reorganization energy for recombination is unlikely to differ significantly between the two solvents. The observed change in the charge recombination rate is therefore most likely linked to differences in the solvent reorganization energy. A dielectric continuum picture of solvent reorganization ($\lambda_s$) would dictate that $\lambda_s$ is larger for NM than for DCM and therefore back electron transfer in DCM is probably in the Marcus inverted region.

Excited state characterization of ReEBA using DFT calculations supports the interpretation of the experiments. The frequency difference of all examined vibrational modes was calculated, and very good agreement was found between the experimental and DFT data (Table 5.5). To quantify the changes in the electron density in different regions of the complex between different excited states, Mulliken charge analysis was used (Table 5.6). A charge of 0.92 electrons is computed to be transferred from the 3DMABN ligand to the rest of the molecule, mostly to the DCEB ligand (Table 5.6) in the DFT analysis.
Table 5.6. Computed Mulliken charges at different moieties of the ReEBA and ReEB compounds for the ground state (S0) and the lowest energy triplet excited state (T1) in DCM and in NM and the charge changes (T1-S0).

<table>
<thead>
<tr>
<th>Moieties</th>
<th>S0</th>
<th>T1</th>
<th>T1-S0</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<tr>
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<tr>
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<tr>
<td>PhCN</td>
<td>0.19</td>
<td>0.24</td>
<td>0.05</td>
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To assess the amount of charge transferred between the ligands in the LLCT state, the C=O peak frequency shifts can be compared to those reported for fully reduced compounds with similar structure. A [Re(CO)$_3$Cl(dcbpy)] complex, where dcbpy is 4,4’-dicarboxy-2,2’-bipyridine, attached to a CdSe quantum dot via carboxylate group was studied by Lian and coworkers. Electron injection from the quantum dot to the complex was observed upon electronic excitation. The complex reduction, with the electron residing
on the dcbpy ligand, was accompanied by a downshift of the C≡O frequencies. The values of the downshift, 18, 32 and 22 cm\(^{-1}\) for \(v_{as1}(C≡O)\), \(v_{as2}(C≡O)\) and \(v_{ss}(C≡O)\), respectively, resemble closely the values found for ReEBA in the LLCT state (Table 5.4). Grills and coworkers prepared reduced [Re(bpy)(CO)\(_3\)(CH\(_3\)CN)] species in water using pulse radiolysis.\(^{146}\) The C≡O frequency shifts due to the reduction, 26 cm\(^{-1}\) for \(v_{ss}(C≡O)\) and 32 cm\(^{-1}\) for \(v_{as}(C≡O)\), are again very similar to those observed in this work for the LLCT state.

There is also a considerable amount of spectroelectrochemistry data for Rhenium tricarbonyl diimine complexes in the literature, where the \(v(C≡O)\) frequencies in the reduced complexes have been measured. The one-electron reduced species show a shift of the \(v_{ss}(C≡O)\) peak by ca. 27 cm\(^{-1}\).\(^{147-150}\) This value also matches well the \(v_{ss}(C≡O)\) frequency shift observed for ReEBA (24 cm\(^{-1}\)), supporting the assignment of its lowest energy excited state as the LLCT state, featuring a nearly full electron transfer from the 3DMABN ligand to the DCEB ligand. Thus, a range of data reported in literature is in agreement with the assessment that the LLCT state in ReEBA features charge separation exceeding 0.9 of electron charge.

The nature of the LLCT state of ReEBA can be understood well by using a previously developed three-state state coupling model (Figure 5.6).\(^{21}\) In this model, three electronic states were assumed: a pure MLCT (Re→bpy or DCEB) state, a full-electron CT (L→bpy or DCEB) state, and an ideal triplet (\(^3\)IL) state fully localized on the L ligand. Mixing of these three states results in the formation of the characteristic states of the complex. The \(^3\)IL state is weekly coupled to the other two states.\(^{21}\) The pure MLCT state and full electron CT state are coupled as both states feature electron transfer to bpy or DCEB; the coupling strength is determined by the spatial overlap of the wave functions for
the two ideal states. This coupling is very strong in Re4DMABN because of the quinoidal resonant structure on the 4DMABN ligand. As a result, the mixed state is lowered in energy substantially but has a significant contribution from both MLCT and CT states. The MLCT and CT state coupling in Re3DMABN is much weaker compared to that in Re4DMABN, due to a lack of quinoidal resonant structure, resulting in a smaller shift of the mixed state energies (Figure 5.6). Consequently, the $^3$IL state of 3DMABN is the lowest energy state in Re3DMABN in DCM. By placing two electron-withdrawing carboxyethyl groups on the bpy ligand, the MLCT and CT state energies of ReEBA were lowered with respect to those for Re3DMABN, as DCEB is a stronger electron acceptor than bpy. Note that the CT state energy was lowered more dramatically than the MLCT state, as the CT state features a larger charge separation distance. Increased energy gap between the MLCT and CT states, together with their weak mixing, facilitates formation of the mixed LLCT state that has mostly CT character. Indeed, the overall experimental and computational results indicate that the lowest energy state for ReEBA is characterized by ca. 92% LLCT character.
Figure 5.6. A three-state model describing a charge-transfer extent in Re4DMABN, Re3DMABN, and ReEBA in the DCM solvent.

5.5. Conclusions

The excited-state dynamics of ReEBA and ReEB were studied in DCM and NM solvents using time-resolved infrared and electronic spectroscopy and DFT analysis. The lowest energy excited state of ReEBA was assigned to a full-electron (3DMABN→DCEB) LLCT state, on the basis of experimental and computational data summarized here: (1) The luminescence quantum yield of ReEBA is two orders of magnitude smaller than that in ReEB, indicating that the MLCT state luminescence is quenched by formation of the LLCT state. The lifetime of the lowest energy excited state of ReEBA decreases dramatically with an increase in solvent polarity, which is indicative of forming a strongly-polarized state. (2) Characteristic changes in the vibrational frequencies of the excited state, including a large down shift of the C═O modes, the absence of a C═N 3IL state peak at ca. 2130 cm⁻¹, and changes of ν(C═O) and ν(bpy) modes, agree well with the formation of the
(3) DFT calculations predict that the amount of charge transferred from the 3DMABN ligand, largely to the DCEB ligand, in the lowest energy excited state is ca. 0.92 of electron charge. Note that formation of a nearly pure LLCT state (about 92%) was accomplished by tuning the redox properties of the electron accepting ligand (DCEB) and simultaneously decoupling the redox active group of the electron donating ligand (3DMABN) from the metal. This molecular engineering strategy permits the design of compact transition metal complexes that feature excited states with essentially full-electron LLCT states.

5.6. Acknowledgment.

Support by the National Science Foundation (CHE-1012371) is gratefully acknowledged. Tod Grusenmeyer performed the synthesis of the Re compounds and ns transient absorption and fluorescence measurements. Zheng Ma and Peng Zhang performed the excited state DFT calculations and charge analysis for the Re complexes.
Chapter 6. Electron Transfer Rate Modulation in a Compact Re(I) Donor-Acceptor Complex

The work presented in this chapter has been published in the following paper:


6.1. Overview

Photoinduced electron transfer (PET) processes have been extensively studied for a variety of applications such as dye-sensitized solar cells, CO$_2$ reduction,$^{15}$ catalytic water oxidation and proton reduction.$^{13-14}$ The control of the PET rate was often approached through structure modification on the molecular system of interest. Because of their well-defined structures and synthetically tunable excited state properties, rhenium complexes have been an excellent system for such studies.$^{21-22, 131, 137-138, 151}$ Modification of one or more ligands can result in big differences in the excited state electron transfer properties. Beside the chemical modifications, optical modulation of the electron transfer (EIT) rate has also been demonstrated.$^{47,48}$ Mid-IR modulation of electron transfer rates is attractive, as it is chemically innocent, simple to control, and potentially mode specific. For systems with uniquely defined group vibrational modes, modulation of electron transfer rates following excitation of particular modes provides fundamental insight into the degree to which these modes are coupled to the electron transfer process.

The PET process in a donor-bridge-acceptor (DBA) assembly,$^{47}$ featuring guanosine-cytidine (GC) hydrogen-bonding bridge moiety, is found to be dependent on the
presence of the vibrational excitation of the bridge vibrations. The mechanism of this modulation was proposed to be a weakening of the hydrogen bonding or distortion of the bridging π electron system by the vibrational excitation.

Modulation of the electron transfer rate between metal and the molecules adsorbed at the metal surface was reported.\textsuperscript{152-153} It is found that intramolecular vibrations of the molecules, such as NO and C\textsubscript{140}, are strongly coupled to the electronic degrees of freedom, promoting the electron transfer reaction. Theoretical findings indicate that EIT kinetics can be changed by controlling the coherence of inelastic tunneling pathway interferences, creating a molecular analogue of the double-slit electron transmission experiment.\textsuperscript{98, 136, 154-157}

In systems with two interfering EIT coupling pathways, the excitation of a pathway-specific bridge vibration, which may induce electron-vibration energy exchange, labels the ET pathway and therefore modifies pathway interferences.\textsuperscript{97-98, 136, 154-157}

Here, we present another molecular system with the EIT rate tunable by the mid-IR radiation, in which the rate of charge separation is enhanced upon vibrational excitation.

Recently we reported a compact Re(I) compound (ReEBA, Scheme 6.1) that features fast photoinduced electron transfer with ca. 10 ps time constant between the 3DMABN and DECB ligands,\textsuperscript{22} where 3DMABN and DCEB denote 3-dimethylaminobenzonitrile and 4,4'-(dicarboxyethyl)-2,2'-bipyridine respectively. The charge separation process occurs as a transition from an initially formed triplet metal-to-ligand charge transfer (MLCT) excited state to a ligand-to-ligand charge transfer (LLCT) state; the LLCT state features almost a full-electron transfer from 3DMABN to DCEB. The ReEBA complex has several convenient IR modes that can be used either to track
formation of the charge separated (LLCT) state or to pump in an attempt to modulate the EIT rate.

![Scheme 6.1. Structure of the Re\(^{(CO)}_3(DCEB)(3DMABN)\) compound, referred to as ReEBA.](image)

We report the study of modulation of the rate of charge separation in ReEBA using 3-pulse UV-pump – IR-pump – IR-probe spectroscopy (Sections 6.3.1-6.3.3). Vibrational coupling of the mode excited by IR-pump, the tag mode, and the vibrational reporter is found to be contributing to the signals measured in the 3-pulse experiments, which makes the data analysis more complicated. In addition, vibrational energy transport from the tag mode to the reporter site contributes to the 3-pulse signals. Therefore, the energy transport process was carefully studied using the relaxation-assisted 2DIR spectroscopy (RA 2DIR, Section 6.3.4).\(^{88}\) Kinetic modeling of the 3-pulse measurements is given in Section 6.3.5.

**6.2. Experimental Details**

The detailed description of the IR-perturbed TRIR spectrometer is presented in Chapter 3.6. The 2DIR spectrometer used in this chapter is described in Chapter 3.7.

Detailed quantum chemistry method is presented in Chapter 3.8.
6.3. Results and Discussion

6.3.1. Selection of the Molecular System.

The ReEBA compound (Scheme 6.1) was selected for the study of the electron transfer rate modulation because it features fast charge separation rate and has a range of convenient vibrational modes (Figure 6.1). Using a combination of transient infrared (UV-pump – IR-probe, TRIR) and transient absorption (UV-pump – vis-probe, TA) spectroscopies and DFT computations, it has recently been shown that an essentially full-electron ligand-to-ligand (3DMABN → DCEB) charge transfer (LLCT) state is formed in ReEBA upon excitation at 402 nm. A triplet MLCT state formed within 200 fs after the excitation is accompanied by significant frequency shifts of many vibrational modes in the complex (Figure 6.2). For example, the stretching modes of the 3 facial carbonyls

![Figure 6.1. Linear FTIR absorption spectrum of ReEBA in DCM measured at 9 mM concentration in the sample cell with 50 μm path length.](image)

(symmetric stretch at 2046 cm\(^{-1}\) and two asymmetric stretches appearing at ca. 1949 cm\(^{-1}\)) are known to be sensitive to the charge of the metal center due to back bonding. These
modes shift to higher frequencies in the MLCT state, reflecting an increase in positive charge on the Re center, as apparent in the TRIR spectrum measured at 1 ps delay (Figure 6.2). Small up-shift of the three carbonyl stretching modes is due to vibrational cooling in the MLCT state, which occurs with characteristic time of 17 ps. The stretching mode of the cyano group appearing at 2258 cm\(^{-1}\) in the ground state is shifted to 2240 cm\(^{-1}\) in the MLCT state. The C=O stretching modes of the ester in the DCEB ligand, appearing at ca. 1735 cm\(^{-1}\), is shifted to lower frequencies in the MLCT state by ca. 35 cm\(^{-1}\), indicating an increased negative charge on the ligand. The ring stretching mode of the DCEB ligand (\(\nu(bpy), 1610\) cm\(^{-1}\)) is also shifted to lower frequencies by ca. 60 cm\(^{-1}\) and its IR intensity increases by ca. 10 fold. The experimental frequency shifts and DFT calculations indicate that the triplet MLCT state features a charge shift of about half of an electron from the Re center and the DCEB ligand, which is similar to that found in other Re\(^{I}\) tricarbonyl complexes.

The MLCT state is converted to the LLCT state with a 10 ps characteristic time. The growth of \(\nu_{SS}(CO)\) at 2023 cm\(^{-1}\) and \(\nu_{AS}(CO)\) at 1910 and 1930 cm\(^{-1}\) and concomitant decay of the peaks at 2075, 1990, and 2240 cm\(^{-1}\) indicate the MLCT to LLCT conversion. The ester carbonyl peak of the DCEB ligand (1700 cm\(^{-1}\)) is shifted further to lower frequencies by ca. 18 cm\(^{-1}\), indicating an increase of a negative charge at the ester sites in the LLCT state. The DCEB ring stretching mode frequency (ca. 1540 cm\(^{-1}\)) changed little, but its IR intensity increases by ca. 18% in the LLCT state, suggesting that the negative charge at the bpy moiety changes little between the two states. The \(\nu_{SS}(CO)\) peak of the LLCT state found at 2023 cm\(^{-1}\) is very narrow and has a large extinction coefficient (7600
M⁻¹ cm⁻¹); this makes it a good probe for detecting the amount of the LLCT states formed in the 3-pulse measurements.

Figure 6.2. Transient infrared spectrum of ReEBA in DCM at selected time delays (see inset) following the 402 nm excitation. The inset shows enlarged spectra at ring stretching region.

6.3.2. Design of the 3-pulse Experiment.

The UV-IR-IR 3-pulse experiments use UV radiation at 402 nm to initiate the electron transfer process. After a delay time, $t_1$, an IR-pump pulse targeting specific spectral region is introduced to perturb the EIT process. The amount of the LLCT state formation is tested by the IR probe pulse as a function of the second time delay, $t_2$, between the IR pump and IR probe (Figure 6.3). A vibrational band most sensitive to formation of the LLCT state should be selected for probing. As mentioned above, the symmetric stretch of the three facial carbonyl groups, $\nu_{\text{SS}}$(CO), featuring in the LLCT state a narrow peak at 2023 cm⁻¹ with a large extinction coefficient of 7600 M⁻¹ cm⁻¹, is convenient for tracing the LLCT state formation (Figure 6.2). Several vibrational modes were tested for their ability
of modulating the EIT rate, including the CN stretching mode and ring stretching mode of the bpy located in the ground state at 2260 and 1610 cm\(^{-1}\), respectively, but a sizable rate modulation is found only for the bpy ring mode excitation; these experiments are described in detail in this report. The IR pump pulse was centered at the peak at 1540 cm\(^{-1}\), which belongs to the bpy stretching mode in the MLCT state (Figure 6.2).

![Figure 6.3](image)

**Figure 6.3.** Pulse sequence used in the 3-pulse experiments.

The 3-pulse transient spectra represent the difference between the transient IR spectra with and without the IR pump; they are recorded by optical chopping of the IR pump pulses at half the laser repetition rate. The 3-pulse transient spectra were measured at several \(t_2\) delays and at two \(t_1\) delays of 2 and 40 ps. At the small \(t_1\) delay of 2 ps, the initially formed MLCT state still did not convert to the LLCT state and the EIT rate modulation by the IR pump can occur. On a contrary, at \(t_1\) of 40 ps, which is much larger than the time constant of the LLCT state formation (10 ps), essentially all excited complexes are in the LLCT state and no rate modulation can be observed. Thus, by comparing the 3-pulse transient spectra and transient kinetics at \(t_1 = 2\) ps and at 40 ps, the EIT modulation features can be identified. To map the kinetics of the LLCT state accumulation during \(t_2\) delay time, the 3-pulse transient kinetics were measured at specific
wavelengths characteristic for formation of the LLCT state (Figure 6.4). Note that the rate modulation is observed cumulatively via observation of a different amount of the LLCT state accumulated over some time interval. The IR-pump – IR-probe spectra have also been measured under the same experimental conditions as the 3-pulse spectra by blocking the UV excitation beam. The IR-pump – IR-probe spectra serve as a reference to help identify the IR-pump – IR-probe contributions to the 3-pulse signals.

Figure 6.4. Schematic representation of the expectations in the 3-pulse experiments. Dynamics of the LLCT state formation without (blue curve) and with (red curve) IR pump are shown, assuming that the EIT rate increases with IR pump.

6.3.3. Results of the 3-pulse Measurements

Figure 6.5A shows the 3-pulse transient spectrum (black) measured at small $t_1$ time delay of 2 ps and $t_2 = 2$ ps. Note that the IR pump spectrum was centered at 1540 cm$^{-1}$, while the IR probe was scanned between 1940 and 2080 cm$^{-1}$. For the $t_1$ delays much smaller than the MLCT$\rightarrow$LLCT reaction time constant (10 ps), the MLCT state is the dominant excited state in the system. In addition, the transient spectrum measured at the
same experimental conditions but with the UV pulses blocked, referred to as the IR-IR transient spectrum, is shown with a red line. Several spectral features can be assigned by comparing the two spectra. Because the bleach peak at 2050 cm$^{-1}$ and the absorption peak at 2046 cm$^{-1}$ are similar in both spectra, they do not require UV excitation and represent the 1600-1610 / CO$\text{SS}$ cross peak in the ground electronic state. The cross peak consists of the ground state bleach at $v_{\text{SS}}$(CO) and absorption to the combination band of 1600-1610 modes and CO$\text{SS}$, that is observed at $v_{\text{SS}}$(CO) – $\Delta_{1600/\text{CO}}$ frequency, where $\Delta_{1600/\text{CO}}$ is the off-diagonal anharmonicity of the two modes.
Figure 6.5. A. 3-pulse and IR-pump – IR-probe transient spectra of ReEBA at $t_1 = 2$ ps, $t_2 = 2$ ps, both measured at the same experimental conditions. B. Transient 3-pulse kinetics measured at 2023 cm$^{-1}$ and $t_2 = 2$ ps. The red curve shows the fit with a single exponential function. C. The difference between 3-pulse and IR-pump – IR-probe transient spectra measured at $t_1 = 40$ ps, $t_2 = 2$ ps and its fit (red) using the Lorentzian profile for the bleach peak with the width of 7.4 cm$^{-1}$ (fwhm) that matches the peak at 2022.4 cm$^{-1}$ in Figure 6.2, and Gaussian profile for the transient absorption peak centered at 2017.3 cm$^{-1}$ with the width of 24 cm$^{-1}$ matching the peak at 1540 cm$^{-1}$. The bleach and absorption components are shown with green lines. The IR excitation frequency in the measurements was 1540 cm$^{-1}$.

The spectral features at 2023 and 2015 cm$^{-1}$ are observed only in the 3-pulse spectra. The bleach at 2023 cm$^{-1}$ matches the v$_{SS}$(CO) peak in the LLCT state, observed in the TRIR measurements (Figure 6.2); its appearance in the 3-pulse spectra can indicate the modulation of the rate of charge separation by the IR excitation. However, together with the negative peak at 2023 cm$^{-1}$, there is a positive peak at 2015 cm$^{-1}$; the appearance of the peak pair can be explained as the vibronic coupling signal of the bpy stretching mode (1540 cm$^{-1}$) and v$_{SS}$(CO) (2023 cm$^{-1}$) in the LLCT state. The relation of the signal at 2023 cm$^{-1}$ to the LLCT state is confirmed by the 3-pulse measurements where the $t_2$ delay is kept constant at 2 ps, while the $t_1$ time is scanned (Figure 6.5B). The signal at 2023 cm$^{-1}$ grows with the 8.4 ± 2 ps time constant indicating that it belongs to the LLCT state, as it matches well the rate of the charge separation (10 ± 1 ps).

The 3-pulse and IR-pump – IR-probe spectra were also measured at a larger $t_1$ time delay of 40 ps (not shown) and $t_2 = 2$ ps; at such $t_1$ values the majority (98%) of the MLCT states were converted to the LLCT state and no modulation of the EIT rate is possible. Similar peaks at 2023 and 2015 cm$^{-1}$ were observed in these two measurements. The difference spectrum between the 3-pulse and IR-pump – IR-probe spectra measured at $t_1 = 40$ ps is shown in Figure 6.5C. The best fit is shown with red line (see Figure 6.5 caption).
While the peaks at 2023 and 2015 cm\(^{-1}\) are observed in the 3-pulse transient spectra at both small and large \(t_1\) delays, the kinetic traces at 2023 cm\(^{-1}\) at small and large \(t_1\) delays show dramatic differences (Figure 6.6A). At \(t_1 = 40\) ps, the kinetics at 2023 cm\(^{-1}\) shows an early time decrease with a maximum at ca. 6 ps; the signal then decays back to the baseline. However, at \(t_1 = 2\) ps, the kinetics does not show any clear decrease at the early time, but also decays to the baseline. The data indicate that the \(t_1 = 2\) ps kinetics has an additional contribution and since at \(t_1 = 40\) ps no EIT modulation signal is expected, the difference between these two kinetic traces may be due the EIT rate modulation effect. The difference between the two kinetics (Figure 6.6B) shows a rise followed by the decay, as expected for the EIT rate modulation dynamics (Figure 6.4); its modeling is discussed in Section 6.3.5.

![Figure 6.6. A. The 3-pulse \(t_2\) kinetics measured at 2023 cm\(^{-1}\) at two \(t_1\) delays: 2 ps (blue) and 40 ps (red). A normalization factor of 1.2 was applied to the kinetics curve at \(t_1 = 40\) ps to match the values at \(t_2\) close to zero with those of the kinetics at \(t_1 = 2\) ps. B. The difference (green) between the two kinetics shown in panel A. The red curve represents the modeling, with the equation \(S(t_2) = A \exp(-k_1 t_1) \times QY[\exp(-k_1 t_2) - \exp(-k_2 t_2)]\) where \(QY\) denotes the vibrational excitation probability (MLCT*/MLCT), evaluated to be 3% and \(A\) is the maximum of the LLCT peak at 2023 cm\(^{-1}\) (in mOD) formed under the actual conditions of both.\]

\[\]
2-pulse and 3-pulse experiments. The $k_1$ rate constant of $(10 \text{ ps})^{-1}$ was used in the modeling. The $k_2$ value of $(7.8 \text{ ps})^{-1}$ was obtained from the fit.

### 6.3.4. Mode Coupling and Relaxation-Assisted 2DIR Measurement.

The 3-pulse spectra clearly show signals that correspond to the vibrational coupling in the ground electronic and LLCT states. To better understand these contributions and to measure the coupling strength of the modes and energy transport dynamics between the ligands, relaxation-assisted 2DIR measurements were performed. The relaxation-assisted 2DIR (RA 2DIR) method relies on vibrational energy transport in molecules that originates from relaxation of the initially excited tag mode. Instead of the direct perturbation of the reporter mode frequency by excitation of the tag observed in traditional 2DIR, the RA 2DIR method relies on delivery of the excess energy introduced by the tag excitation to the region in the molecule where the reporter is located. The excited tag mode relaxes to other modes in the molecules and the excess energy is propagating along the molecular chain as a part of the energy dissipation process. Once it reaches the reporter mode site, the reporter mode frequency is perturbed and the cross-peak appears at the intersection of the tag and reporter mode frequencies. Cross peak enhancements as large as 27-fold were observed in the waiting time traces.\textsuperscript{87} The RA 2DIR method provides an important new observable, the energy transport time, that can be a useful structural constraint.\textsuperscript{158-159} Due to through-bond connectivity observed for numerous molecules,\textsuperscript{86, 160-162} a smaller $T_{max}$ values are found for the vibrational modes that are closer to the initially excited mode, permitting mode assignment based on the $T_{max}$ values.

The relaxation-assisted 2DIR measurements were performed focusing on the cross peaks between the $\nu(bpy)$ and $\nu_{SS}(CO)$ modes. Figure 6.7 shows a 2DIR magnitude
spectrum of ReEBA measured in the (1500 – 1700) / (1950 – 2070) cm\(^{-1}\) spectral region, featuring several cross peaks. A clear cross peak is observed at ca. 1605 / 2045 cm\(^{-1}\). Because \(\nu(bpy)\) is close in frequency to \(\nu(ph)\) (1610 and 1600 cm\(^{-1}\), respectively) their cross peaks with \(v_{SS}(CO)\) are not spectrally resolved. However, the waiting-time dependences for these two cross peaks, plotted in Figure 6.8, have different \(T_{\text{max}}\) values, confirming that both ring modes are coupled to \(v_{SS}(CO)\). The \(T_{\text{max}}\) values indicate the energy transport time from the excited vibrational mode, \(\nu(bpy)\) or \(\nu(ph)\), to the region where the probed mode is located. The \(T_{\text{max}}\) value for the \(\nu(bpy) / v_{SS}(CO)\) (3.5 ps) is smaller than that for the \(\nu(ph) / v_{SS}(CO)\) (5 ps), as the bpy is located closer to the metal carbonyls than the phenyl ring of 3DMABN. The kinetics of the \(\nu(bpy) / v_{SS}(CO)\) waiting time matches well the 3-pulse kinetic trace at 2023 cm\(^{-1}\), measured at \(t_1 = 40\) (Figure 6.8, green line). The match indicates strongly that the 3-pulse kinetics vs. \(t_2\) delay measured at \(t_1 = 40\) ps at 2023 cm\(^{-1}\) originates from the \(\nu(bpy) / v_{SS}(CO)\) coupling in the LLCT state.

**Figure 6.7.** 2DIR spectrum of ReEBA in DCM measured at 3 ps waiting time. The first two excitation pulses were centered at 1600 cm\(^{-1}\) and the third pulse and the local oscillator were centered at 2040 cm\(^{-1}\). The linear spectrum of ReEBA is shown in the attached panels.
Figure 6.8. Waiting-time dependences of the and $\nu$(bpy)/$\nu$ss(CO) (green) and $\nu$(ph)/$\nu$ss(CO) (black) cross peaks in the ground electronic state measured via RA 2DIR. The IR pulses, the first two and the third, were centered at 1600 and 2040 cm$^{-1}$, respectively. The normalized 3-pulse $t_2$ kinetics measured at 2023 cm$^{-1}$ at 40 ps delay (red curve in Figure 6.6A) is shown for comparison.

6.3.5. Data Analysis and Modeling.

A kinetics scheme used to model the experimental results is shown in Figure 6.4. The whole process is described as follows. The UV pulse excites ca. 5% of the complexes into the MLCT state, which converts into the LLCT state with a time constant $k_1$ of 10 ps. Introducing the IR excitation of the ring stretching mode of bpy (with ca. 3% excitation probability) results in an alternative reaction pathway that occurs from the vibrationally excited MLCT state, denoted as MLCT*. The respective rate constant, $k_2$, is the only tunable parameter in the scheme. The 3-pulse transient kinetic trace is modeled by taking the difference between the kinetics for these two paths, which represents the difference in the amount of LLCT state with and without IR pump (see Figure 6.6 caption). The best fit modeling kinetics is plotted in Figure 6.6B (red), together with the experimental data (blue). The rate constant ($k_2$) was varied and the best fit was found at $k_2 = (7.8 \text{ ps})^{-1}$ (Figure 6.6B).
Note that the signal amplitude was the main parameter for the fit; the peak amplitude (in mOD) was referenced to the peak amplitude at 2023 cm$^{-1}$ (also in mOD) measured in the UV-pump – IR-probe experiments (as in Figure 6.2). The $k_2$ value obtained by matching the amplitude also reproduces well the time profile of the 3-pulse data. The modeling results indicate that the rate of the LLCT state formation is increased by 28% when the reaction proceeds from the vibrationally excited MLCT state.

![Figure 6.9. Potential energy difference (in eV) between the T1 and T2 states computed along the bpy stretching normal coordinates for the modes at 1544 cm$^{-1}$ (black) and 1576 cm$^{-1}$ (red). $\Delta R$ is the relative displacement of the equilibrium geometry along the normal mode ($\Delta R=0$ corresponds to the T1 state equilibrium structure).](image)

Time-dependent DFT calculations using a B3LYP functional were carried out to map the potential energy surface of T2 (MLCT) and T1 (LLCT) triplet states in ReEBA. The energy difference between the T2 and T1 states along the two bpy stretching modes, 1544 cm$^{-1}$ and 1576 cm$^{-1}$ (both strongly IR active), computed at the equilibrium geometry of the T1 state, was monitored. The scan started from the T1 equilibrium structure and the
results are presented in Figure 6.9. As one can see, the excitation of the bpy stretching modes will bring the two surfaces closer to near degeneracy point, resulting in a faster nonadiabatic electronic transition to from T2 to T1. Particularly, the mode of 1544 cm\(^{-1}\) is more effective in promoting the MLCT to LLTC transition. These results suggest that the bpy stretching modes are strongly coupled to the EIT reaction coordinate.

### 6.4. Conclusions

Several factors affected the data recorded in this study. One is related to degradation of the sample under UV radiation. Note that while the sample volume was substantial (>3 mL) and minimal overall degradation was observed after the experiments, the UV power had to be small to avoid precipitation on the optical windows. Even with the use of the flow cell the maximum power of the UV pump was rather low allowing to generate only less than 5% of excited molecules in the excited area of the sample. Lower UV power resulted in smaller 3-pulse signals. Another complication is associated with the presence of the vibrational and vibronic coupling signals, and the latter was masking the EIT modulation effect. In addition to vibronic coupling that is the strongest at zero time delay time between the IR pump and IR probe pulses, the energy transport dynamics originated from relaxation of the IR-pumped mode also contributed to the 3-pulse spectra and kinetics. Independent characterization of the energy transport performed using the RA 2DIR method demonstrated that the transport dynamics is similar in the ground and excited states.\(^{163}\)

Comparison of the 3-pulse signals measured at small and large \(t_1\) delays clearly shows an additional contribution attributed to the EIT modulation effect. Although the EIT modulation signals are not very large, the EIT rate change due to modulation is sizable (~28%), because of the small vibrational excitation probability (ca. 5%). Note that the bpy
stretching mode, found to modulate the EIT rate, is capable of affecting the Re – bpy distance. It vibrational relaxation populates most likely other modes in the bpy which also can affect the Re-bpy coordination bonds. Because the short lifetime of the bpy stretching mode, the modes accepting energy from the initially excited bpy stretching mode are likely contributing to the modulation effect. The EIT time constant of 10 ps is too large to assess which specific mode is affecting the rate the most. Theoretical modeling demonstrates that bpy stretching modes are capable of modulating the EIT rate in ReEBA; more involved calculations are ongoing and will be reported elsewhere.

6.5. Acknowledgment.

Support by the National Science Foundation (CHE-1012371) is gratefully acknowledged. Tod Grusenmeyer performed the synthesis of the Re compounds and ns transient absorption and fluorescence measurements. Zheng Ma and Peng Zhang performed the excited state DFT calculations for the Re complexes.
Chapter 7. Band-Selective Ballistic Energy Transport in Alkane Oligomers: Towards Controlling the Transport Speed

The work presented in this chapter has been accepted for publication:


7.1. Overview

Vibrational energy transport in molecules is important for a variety of fields, including nanotechnology, chemistry, and biochemistry. Detailed understanding of the vibrational energy transport on a molecular level and ability of manipulating its dynamics is essential for a variety of applications such as designing efficient energy transport schematics for controlling chemical reactions as well as providing efficient cooling in microscopic and macroscopic molecular systems, such as nanowires. Two mechanisms can be used to describe vibrational energy transport in molecules, diffusive mechanism and ballistic mechanism. Diffusive energy transport involves Brownian-like energy exchange IVR steps, while ballistic energy transport assumes a vibrational wavepacket propagation through delocalized molecular vibrations, and can be fast and efficient. To better understand ballistic energy transport and pathways for efficient energy dissipation, the through-chain energy transport in studied in a series of oligomers using relaxation-assisted two-dimensional infrared (RA-2DIR) method
The recently developed RA-2DIR method\textsuperscript{86,164} has proven to be an effective tool for studying vibrational energy transport on a molecular scale.\textsuperscript{87,158,165-169} Vibrational excitation of a tag mode with short mid-IR laser pulses is used to introduce the excess energy into the molecule and initiate energy transport (Figure 7.1A). Additional mid-IR laser pulses were applied to probe the reporter transitions at controlled time delay $T$, referred to as a waiting time, following the excitation pulses. At short waiting times the tag/reporter cross-peak amplitude is determined by their coupling strength; the cross peak is weak if the distance between the tag and the reporter is large (Figure 7.1B). At longer waiting times, the excited tag relaxes to other modes in the molecule and the excess energy propagates within the molecule as well as dissipates to the solvent, although the latter process occurs slowly with a characteristic time of 15-20 ps.\textsuperscript{124} When the excess energy reaches the reporter site, exciting the low-frequency modes there (Figure 7.1A), the reporter mode frequency changes, causing an increase of the tag-reporter cross-peak amplitude (Figure 7.1C).\textsuperscript{164} Thus, the waiting time dependence of the cross-peak amplitude provides a direct measure of the energy transport dynamics in the molecule between the tag and the reporter. By measuring the energy transport times for oligomers of different chain lengths, the speed of the energy transport via the chain can be determined.\textsuperscript{166}

The dynamics of the energy transport via oligomeric chains in series of CH$\textsubscript{n}$-a, CH$\textsubscript{n}$-s (Figure 7.1D),\textsuperscript{53} and polyethylene glycol (azPEG$n$)\textsuperscript{166,170} compounds were recently measured using the RA 2DIR technique. In those studies, the N≡N stretching mode of the azido moiety ($\nu$(N≡N)), attached to one end of the chain was used as a tag to initiate the energy transport and a number of vibrational modes, located at the opposite end of the chain, were used as reporters for the energy arrival. It was found that the energy transport
via alkane chains initiated by the $v(\text{N}=\text{N})$ tag proceeds ballistically with a speed of 14.4 Å/ps, while the energy transport within the succinimide ester end-group moiety occurs diffusively with the effective speed of 1.3 Å/ps. The speed of the energy transport via PEG chains, also initiated by the $v(\text{N}=\text{N})$ tag, was measured at 5.5 Å/ps, which is much smaller than that in alkanes. The energy transport in a series of perfluoroalkane oligomers, featuring rod-like chain structures, was also found to be ballistic but with an even slower transport speed of 3.9 Å/ps; it should be noted that the transport was initiated by the $v(\text{C}=\text{O})$ tag. The large variation of the ballistic transport speeds is likely caused by the differences in the chain bands involved in the transport in oligomers of different primary structures.

7.2. Experimental Details

7.2.1. Experimental Method.

The detailed description of the fully automated 2DIR spectrometer is presented in Chapter 3.7.

7.2.2. Sample Preparation.

Two series of compounds ($\text{CH}_n$-a and $\text{CH}_n$-s), featuring alkane chains of different length were studied (Figure 7.1A). The $\text{CH}_n$-a and $\text{CH}_n$-s compounds with $n = 5, 10, 15$ were synthesized according to the reported procedures. The CH3-s compound was purchased from Quanta BioDesign and used as received. For spectroscopic measurements, the CH$n$-a and CH$n$-s compounds were dissolved in deuterated chloroform at 120 and 40 mM concentration, respectively, and placed into a 100 μm thick optical cell with CaF$_2$ or BaF$_2$ windows.
7.2.3. Quantum-Chemistry Calculations.

Detailed quantum chemistry method is presented in Chapter 3.8.

7.2.4. Band Structure Calculations.

Consider an alkane chain with $C_2H_4$ as a unit cell. Introduce 18-dimensional displacement vector $x_k$ for the atoms of the $k$-th unit cell (6 atoms × 3 Cartesian coordinates = 18 degrees of freedom). The Hessian matrix of the system can be splitted into blocks $H(k, n)$, 18-by-18 matrices corresponding to harmonic interaction between $k$-th and $n$-th unit cells. The assumption of translational symmetry leads to relations $H(k + m, n + m) = H(k, n)$. Assuming short-range interaction ($H(k, k + 3) \approx 0$) we can represent the Hamiltonian as

$$H = \frac{1}{2} \sum_k \{ p_k^T M^{-1} p_k + x_k^T A x_k + x_k^T B x_{k-1} + x_k^T C x_{k+1} + x_k^T C x_{k-2} + x_k^T C x_{k+2} \}$$

where $A = H(k, k)$, $B = H(k, k + 1)$, $C = H(k, k + 2)$, $p_k$ is the momentum vector and $M$ is the 18-by-18 diagonal matrix of atomic masses. The choice of the boundary conditions is not significant for the dispersion relations, so for the sake of simplicity we can choose the periodic boundary conditions.

Dispersion Relations. Introducing mass weighted vectors and matrices $y_k = M^{1/2} x_k$, $\tilde{p}_k = M^{-1/2} p_k$, $A_w = M^{-1/2} A M^{-1/2}$, etc., we obtain the equation of motion for $k$-th unit cell as

$$\ddot{y}_k = -A_w y_k - B_w^T y_{k-1} - B_w y_{k+1} - C_w^T y_{k-2} - C_w y_{k+2}$$

(2)
Applying Fourier transform $y_k(t) = \sum_q u_k(q) \exp\{-i\omega(q)t\}$ and using the Bloch theorem $u_k(q) = u(q) \exp\{iaqk\}$, we obtain the equation

$$G(q)u = \omega^2(q) u$$

(3)

where

$$G(q) = A_w + (B_w + B^+_w) \cos(aq) + i(B_w - B^+_w) \sin(aq) + (C_w + C^+_w) \cos(2aq) + i(C_w - C^+_w) \sin(2aq)$$

(4)

and $a$ is a lattice period. Using Eq. 3, the dispersion relations for each mode, $\omega_i(q), i = 1 - 18$, can be obtained expressing eigenmode frequencies as square roots of corresponding eigenvalues of the Hermitian matrix $G(q)$. Based on the symmetry properties of the Hessian matrix, it can be shown that the four lowest frequency bands, $i = 1 - 4$, are acoustic ($\omega_i(0) = 0$), whereas other bands are optical as $\omega_i(0) \neq 0$ for $i = 5 - 18$.

7.2.5. Group Velocity Calculations.

The Hessian matrix for the alkane chain was obtained using the DFT normal mode analysis for CH15-a. To reduce the boundary effects, the matrices $A, B, C$ were determined for the third and fourth cells in CH15-a and nearly identical results were obtained, as expected. The short range approximation is justified by the relation: $||H(k, k \pm 3)||/||H(k, k \pm 1)|| \ll 6 \cdot 10^{-3}$. The lattice period was taken as $a = 3.06$ Å.

Practically, the Hessian matrix does not reveal an ideal translational and rotational symmetry; also the neglected non-zero elements increase the effect of violation of the $G(q)$
matrix symmetry properties. The calculation error in the Hessian leads to the error in the calculated frequencies. The absolute value of the error, $\delta \omega$, is of the same order of magnitude for all bands, although the relative error, $\delta \omega / \omega_l$, increases for the bands with smaller frequencies. Therefore, the low-frequency modes, the acoustic bands, require more careful consideration, which will be a subject for further study. For the optical bands, $\delta \omega / \omega_l \ll 1$, the above mentioned minor symmetry violation is negligible.

Figure 4A shows the lowest energy optical bands, $i = 5 - 14$. The bands appear in the graph in pairs represented by the lines of the same color. For example, the two rocking modes ($i = 5&6$), are shown with black lines, where the first rocking band spans from 730 to 802 cm$^{-1}$ and the second rocking band spans from 802 to 1075 cm$^{-1}$. It is sufficient to plot the band in the wavevector region from 0 to $\pi/a$; for the finite chain length, this portion of the band contains the number of states equal to the number of unit cells. Due to central symmetry of the unit cell, the two bands of the same motion type have exactly the same energy at $q = \pi/a$ and continuous derivative. Thick lines are used to identify clearly the bands of the same motion type. Each thick line comprises two bands, one in the wavevector region from 0 to $\pi/a$, another from $\pi/a$ to $2\pi/a$ (Figure 7.4A and Table 7.1). The group velocity for a narrow range of frequencies centered at $\omega_0(q_0)$ is determined as

$$V(q_0) = (\partial \omega / \partial q)|_{q=q_0};$$

because it is different for different ranges of wavevectors (frequencies), the mean group velocity over a selected range of wavevectors from $q_1$ to $q_2$ is computed as:

$$< V_b > = (q_2 - q_1)^{-1} \int_{q_1}^{q_2} V(q)|dq.$$

(5)
The mean group velocity corresponding to the whole \(i\)-th band is defined as:

\[
V = \frac{\langle a/\pi \rangle}{\int_0^{\pi/a} |\partial \omega_i/ \partial q|dq}.
\]

The group velocities computed for each optical band \((i = 5-14)\) as a whole are given in Table 7.1.

### 7.2.6 Mode Coupling Evaluation

**Azido end group.** The symmetry affects the coupling between the energy receiving modes and the chain bands. Alkane chains in solution can have anti or gauche conformations at every carbon site.\(^{166}\) The DFT calculations used to evaluate the bands were computed for the molecules with all-anti conformation of the chain, which features a symmetry plane. As the nearest CH\(_2\) group interactions are dominant (vide supra), the dependence of the band frequencies on the anti vs. gauche conformation is small and the all-anti conformation of the chain is expected to be representative for the chain bands in solution. Indeed, the computed bands match well the reported experimental bands (Table 7.2) and similar band frequencies were found for a variety of chain conformations. Because of the nearest group interaction dominance, the coupling of the end group modes to the chain states is mostly affected by the conformation at the chain carbon closest to the end group. For example, if the azido group is in the anti-conformation, the azido-group stretching modes (\(\nu(N=N)\) and \(\nu(N-C)\)) are fully symmetric with the motion occurring within the symmetry plane. Therefore, they can only be coupled to the symmetric chain states, the CH\(_2\) wagging and C-C stretching, but not to the CH\(_2\) twisting, scissoring, or rocking. Thus, when the azido group is attached to the chain in the anti-conformation, the \(\nu(N=N)\) mode relaxes predominantly into the wagging band while \(\nu(N-C)\) can only relax into the C-C stretching band, which is though far in energy. When the azido group is gauche
to the chain the \( \nu(N=N) \) mode is also coupled to the CH\(_2\) twisting band, whereas the \( \nu(N-C) \) mode is coupled to the CH\(_2\) rocking band.

The DFT calculations show that the conformer gauche at the N\(_3\)-chain connection (all other sites were anti), has a slightly lower energy than the all-anti conformer by 86 cm\(^{-1}\). Taking into account the Boltzmann factor and that two gauche conformations are possible, the ratio of the two conformers of gauche vs. anti of 3 is obtained at room temperature. So the gauche conformers at the azido-group site are ca. 3 times more abundant than the anti, which makes the twisting band a major contributor to the \( \nu(N=N) \) mode relaxation.

**Ester end group.** The potential energy surface concerning the succinimide ester orientation with respect to the chain is shallow and a range of conformations along \( \theta \) are thermally accessible at room temperature (Figure 7.5A). A coupling strength for the \( \nu_{as}(NOC) \) with the two stretching modes and three rocking of the chain in the CH\(_3\)-s compound was evaluated as a function of the dihedral angle \( \theta \). The DFT normal-mode calculations with a fixed dihedral angle and optimized all other degrees of freedom were performed at different dihedral angles at a 10 degrees grid. The coupling was evaluated by scanning the masses of the oxygen and nitrogen atoms at the ester using the mass-normalized Hessian and detecting the frequency jump of the \( \nu_{as}(NOC) \) mode frequency when it passes the resonance with other normal mode in the molecule. A somewhat similar approach was used previously where an external electric field strength was varied to shift the energy of one state with respect to another.\(^{173}\) The frequency jump equals to \( 2V \), where \( V \) is the coupling of the two modes. It was evaluated for the two C-C stretching modes at the chain and three rocking modes and the squares were averaged within each mode type.
(Figure 7.5B). Clearly, the v_{as}(NOC) mode is much more strongly coupled to the stretching modes of the chain than to the rocking modes (Figure 7.5B). Taking into account the Boltzmann factor, the graph 5C is obtained. Considering the difference in the density of states, which is inversely proportional to the group velocity, the Fermi Golden rule is used for comparing the rate constants for the v_{as}(NOC) mode decay into the CC stretching vs. CH$_2$ rocking modes of the chain, weighted for all structures (Figure 7.5C). About 13-fold dominance of the relaxation rate into the CC stretching modes is obtained.

7.2.7 Vibrational Relaxation Dynamics Calculations

Vibrational relaxation dynamics was computed using a recently developed method based on a modification of the Marcus theory for electron transfer applied to anharmonic transitions.$^{174-175}$ The theory calculates the rates (Holstein)$^{176}$ of all IVR processes involving three modes ($i\rightarrow j+k$, $i+j\rightarrow k$). Required anharmonic frequencies, third-order anharmonic force constants, and the X-matrix of anharmonic couplings$^{177}$ were computed using the perturbative anharmonic treatment implemented in Gaussian 09. The initial population distribution for all modes was taken to be thermal at room temperature, except for the tag mode, whose initial population was increased by unity. The only free parameter in the calculations, the rate of energy dissipation to the solvent, was taken as (14 ps)$^{-1}$.${}^{124}$
Figure 7.1. A. Diagram illustrating the principles of RA 2DIR spectroscopy. An example of the cross peak between $\nu$(C=O) and $\nu$(N=N) in CH5-a, measured at $T = 1$ ps (B) and it’s waiting time dependence (C) obtained by integrating the individual 2DIR spectra along $\omega_\tau$ axis from 1650 to 1780 cm$^{-1}$. The tag excitation pulses in this measurement were centered at 1710 cm$^{-1}$, while the tag probing pulses were centered at 2100 cm$^{-1}$. D. Structures of the CH$n$-a and CH$n$-s compounds with indicated combinations of tags and reporters. E. Linear absorption spectra of CH5-a, CH15-a, and CH5-s in CDCl$_3$ at 120, 120, and 40 mM concentrations, respectively. The modes used as tags and reporters are indicated.

Table 7.1. Chain band frequencies at $q = 0$ and $\pi$ ($\omega(0)\,$ and $\omega(\pi)$) and the group velocities computed for each band, $\langle|V|\rangle$, and for the specific frequency regions, $\langle|V_b|\rangle$, indicated in Figure 7.4A.

| Band # | Band type | $\omega(0)$, cm$^{-1}$ | $\omega(\pi)$, cm$^{-1}$ | $\langle|V|\rangle$, Å/ps | $\langle|V_b|\rangle$, Å/ps in boxes |
|--------|------------|---------------------|---------------------|-----------------|------------------|
| 5      | $\rho$(CH$_2$) | 733     | 804     | 10.5             | 32.8$^a$          |
| 6      | (black)   | 1082    | 804     | 42.7             | 62$^b$            |
| 7      | $\nu$(CC) | 1138    | 1014    | 33.5             | 66$^a$            |
| 8      | (cyan)    | 1067    | 1014    | 8.8              | 7.6$^a$           |
| 9      | tw(CH$_2$) | 1196    | 1337    | 21.5             |                  |
| 10     | (blue)    | 1328    | 1337    | 4.0              | 11.2$^c$          |
The group velocities measured within the boxes matching the width of the two v(NOC) modes, b the v(N-C) mode, and c the v(N=N) mode.

Table 7.2. Comparison of the DFT computed frequencies for different chain bands with experimentally reported values for polyethylene. The experimental frequencies are presented based on individual peak assignment.

<table>
<thead>
<tr>
<th>Band</th>
<th>Computed chain band frequencies (cm⁻¹)</th>
<th>Experimental frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂ Scissoring</td>
<td>1480.4 – 1516.4</td>
<td>1416, 1440, 1463, 1473</td>
</tr>
<tr>
<td>CH₂ Wagging</td>
<td>1211.9 – 1405.8</td>
<td>1175, 1370</td>
</tr>
<tr>
<td>CH₂ Twisting</td>
<td>1195.6 – 1344.7</td>
<td>1050, 1296</td>
</tr>
<tr>
<td>CC stretching</td>
<td>996.5 – 1138.2</td>
<td>1067, 1133</td>
</tr>
<tr>
<td>CH₂ Rocking</td>
<td>733 – 1082.1</td>
<td>721, 734, 1170</td>
</tr>
</tbody>
</table>

7.3. Results and Discussion

This study is directed at identifying the nature of the chain bands predominantly contributing to energy transport via alkane chains, initiated by various tags in series of the CHₙ-a and CHₙ-s compounds (Figure 7.1D). In addition to the RA 2DIR measurements, we performed theoretical analysis of the transport speeds supported by different optical chain bands and analysis of the relaxation pathways within the oligomers. Several end-group vibrational modes, such as v(N≡N) and v(N=N) of the azido moiety and carbonyl stretches of the carboxylic acid and succinimide ester, served as tags initiating the energy transport via the alkane chain (Figure 7.1D). The tags and respective reporters are indicated in Figure 7.1D; their infrared absorption peaks are shown in Figure 7.1E. Figure 7.1C shows that the C=O/N≡N cross-peak amplitude increases with the waiting time due to the
energy transport from the tag ($\nu(C=O)$) to the $\nu(N=N)$ reporter site and reaches maximum at ca. 4.2 ps. The subsequent decay of the cross peak is associated with dissipation of the excess energy to the solvent.\textsuperscript{166}

The one-dimensional waiting-time kinetics were constructed from the 2DIR data (Figure 7.2A,B) and fitted with a double-exponential function (Figure 7.2A, red lines) to evaluate the $T_{\text{max}}$ value (marked with arrows). Averaged over three measurements per compound, the $T_{\text{max}}$ values were plotted as a function of the tag-reporter distance (Figure 7.2C). The dependence can be fitted well by a linear function and the energy transport speed, calculated as $1/$slope, was obtained at $8.0 \pm 0.3$ Å/ps. Such a high transport speed via the chain suggests that the transport is ballistic.\textsuperscript{52,166}

![Figure 7.2. A. Waiting time dependence of the $\nu(C=O)/\nu(N=N)$ cross-peak amplitude for the indicated CH$n$-a compounds. The fit with a two-exponential function is shown (red lines); the $T_{\text{max}}$ values obtained from the]
fit are indicated by arrows. B. The $T_{\text{max}}$ values plotted as a function of the tag-reporter distance for the CH$n$-a and CH$n$-s compounds for the transport initiated by $\nu$(C=O) and $\nu_{\text{as}}$(C=O), respectively. The linear fit (red lines) resulted in the transport speed of 8.0 ± 0.3 Å/ps for both series. C. Waiting time dependence of the $\nu_{\text{as}}$(C=O)/$\nu$(N=N) cross-peak amplitude for the indicated CH$n$-s compounds at ca. 40 mM concentration. The fit with a two-exponential function is shown (red lines). D. Dependences of the $\nu$(C=O)/$\nu$(N=N) and $\nu_{\text{as}}$(C=O)/$\nu$(N=N) cross peak amplitudes for the CH$n$-a and CH$n$-s compounds, respectively. The fits with exponential decay function (red line) resulted in the characteristic decay distances, $R_0$, indicated in the inset.

Note that the C=O group in the CH$n$-a compounds is directly attached to the alkane chain, so the wavepacket in the chain can be initiated rapidly by the $\nu$(C=O) tag relaxation. This relaxation has to occur through anharmonic interactions as the energy gap between the $\nu$(C=O) and the closest chain band states is substantial (> 230 cm$^{-1}$). The intercept corresponding to a zero chain length in Figure 7.2D is 0.95 ps which is comparable to the $\nu$(C=O) excited-state lifetime measured at 1.2 ps. The match of the two characteristic times suggests that a single IVR step is required to form a wavepacket in the chain. It is not clear, however, which chain bands contribute the most to the transport.

Similar RA 2DIR experiments were performed for the CH$n$-s compounds where the $\nu_{\text{as}}$(C=O) of the succinimide ester served as a tag to initiate the transport and $\nu$(N=N) served as a reporter (Figure 7.2B). The $\nu_{\text{as}}$(C=O) mode (1742 cm$^{-1}$, Figure 7.1E) involves asymmetric motion of the two carbonyls of the succinimide group, and thus is spatially separated from the chain by three bonds. As a result, additional IVR steps following the initial tag relaxation are expected to occur before the excess energy reaches the chain. Indeed, the $T_{\text{max}}$ values for all three CH$n$-s samples are significantly larger (by 3.3 ps) than the respective $T_{\text{max}}$ values for the CH$n$-a samples (Figure 7.2A,B). However, the speed of the energy transport via the chain in CH$n$-s, 8.0 ± 0.2 Å/ps, appears to be the same as the
speed in CHₙ-a (Fig. 7.2C). Interestingly, this speed is different from the speed of transport via alkane chains initiated by the v(N≡N) tag (14.4 ± 2 Å/ps)¹⁶⁶.

Figure 7.3. Rates of all relaxation channels of the v(N≡N) tag (A) in CH₅-a, the vₘd(C=O) tag (B) in CH₅-a, and v(C=O) tag (C) in CH₃-s, normalized in each case by the sum of all respective rate constants (k_i / ∑ k_i).

D. DFT computed energy states of CH₁₅-a (filled symbols) and CH₅-a (opened symbols), both in the all-anti conformation, plotted in the order of ascending energy for each motion type. There are 15 chain states of each motion type for CH₁₅-a, except for v(CC), for which it is 14, which are equally spaced along the j axis. The j-axis for CH₅-a was constructed the same way. The energies of the azido-group modes, v(N≡N)
and v(N-C), are also shown (orange). The boxes, centered at the v(N=N) and v(N-C) mode frequencies, are 150 and 15 cm⁻¹ high, respectively, to indicate the chain states which fall within the full width at 1/e of the maximum of the respective azido-group transition. E. Linear absorption spectra for CH5-a in KBr pellet (blue line) and 1,3,4,6-tetra-O-acetyl-2-azido-2-deoxy-α-D-glucopyranose (α anomer, red line) in deuterated chloroform.

The difference in speed indicates that different chain bands are involved in the energy transport for different types of transport initiation. Theoretical analysis of the vibrational relaxation channels, based on a recently developed Marcus-type theory for the vibrational relaxation rates via anharmonic transitions,¹⁷⁴,¹⁷⁹ was performed for the three tags, v(N≡N), v(C=O), and v_as(C=O), to help identify the most probable chain states involved in the transport. The method uses the mode coupling constants (Vijk) evaluated for the molecule in question by anharmonic calculations within the DFT method (see SI). Note that the DFT calculations were performed for the isolated molecule and its low-frequency modes serve as a bath in the theoretical treatment.¹⁷⁴ The relaxation dynamics calculations show that the v(N≡N) mode decays predominantly into the combination band of the v(N=N) and v(N-C) modes at the azido moiety (Figure 7.3A); the rate of the second fastest decay channel is over ten-fold smaller. The dominance of essentially a single decay channel occurs due to a small number of degrees of freedom at the azido moiety.

To inspect if the v(N=N) and v(N-C) modes energy-match any chain bands, the latter were plotted in the energy ascending order within each motion type for the CH15-a and CH5-a compounds (Figure 7.3D). The v(N=N) mode frequency falls within two chain bands, corresponding to the CH2 wagging and twisting motions (Figure 7.3D). The v(N-C) mode frequency matches the CH2 rocking band of the chain. Importantly, the width of the v(N=N) transition is very large (Figure 7.1&7.3E) with the full width at half maximum
(fwhm) of 123 cm$^{-1}$. As a result, there are many dark chain states within its bandwidth, which provide a large number of relaxation channels (Figure 7.3D, box). The lifetime broadening is proposed as a major reason for the large ν(N=N) linewidth. The lifetime of the excited state can be evaluated as $T_l = \frac{2\pi\sigma}{\omega}$, where $\sigma$ is the fwhm of the transition in wavenumbers and $c$ is the speed of light, resulting in the lifetimes of 44 fs. Note that the ν(N=N) peak in azido-substituted α-D-glucopyranose (α anomer) is much narrower (43 cm$^{-1}$, Figure 7.3E), confirming the importance of the alkane chain states for the broadening. The width of the ν(N-C) transition is small, ca. 12 cm$^{-1}$, resulting in much fewer resonances with the chain states.

In addition to the energy match, the symmetry affects the coupling between the energy receiving modes and the chain bands. DFT calculations showed that the conformer gauche at the N$_3$-chain connection has a slightly lower energy than the all-anti conformer by 86 cm$^{-1}$. Taking into account the Boltzmann factor and twice higher statistical weight of the gauche conformation, we obtain that the gauche conformers at the azido-group site are ca. three-fold more abundant than the anti, which makes the twisting band a major contributor to the ν(N=N) mode relaxation.

Additional refinement for the involvement of different chain bands can be obtained from the comparison of the group velocities supported by each chain band with the experimental transport speeds. Previously the band structure was evaluated for alkane chains using semi-empirical force-field methods and these results are consistent with our DFT analysis (see SI for details). The Hessian matrix of force constants for the alkane chain was obtained from the DFT normal mode analysis for CH15-a. The optical bands, shown in Figure 7.4A, appear in pairs and are represented by the lines of the same color. For
example, the two rocking modes are shown with black lines, where the first band spans from 733 to 804 cm$^{-1}$ and the second band spans from 804 to 1082 cm$^{-1}$. It is sufficient to plot the band in the wavevector ($q$) region from 0 to $\pi/a$; for the finite chain length, this portion of the band contains the number of states equal to the number of unit cells. Due to central symmetry of the unit cell, the two bands of the same motion nature have the same energy at $q = \pi/a$ and continuous derivative. Thick lines are used in Figure 7.4A to identify the bands of the same motion type. Each thick line comprises two optical bands, one in the wavevector region from 0 to $\pi/a$, another from $\pi/a$ to $2\pi/a$ (Figure 7.4A, Table 7.1).

![Figure 7.4. A. Structure of ten lowest-energy optical bands for the alkane chain (labeled) as a function of a normalized wavevector. The boxes match the width of the azido-group stretching modes, $v$(N=N) and $v$(C-](image-url)
N) (similar to that in Figure 7.3D) and the ν(NOC) of the succinimide ester (violet). B. Change of the population numbers at indicated delays after excitation of \( \nu_{\text{ad}}(\text{C}=\text{O}) \) in CH3-s.

The group velocity for a narrow range of frequencies centered at \( \omega_0(q_0) \) is determined as \( V(q_0) = \left( \frac{\partial \omega}{\partial q} \right)_{q=q_0} \). Because the velocity is different for different ranges of wavevectors (frequencies), the mean group velocity over a selected range of wavevectors from \( q_1 \) to \( q_2 \) is computed as:

\[
<V_b> = \frac{(q_2 - q_1)^{-1}}{\int_{q_1}^{q_2} |V(q)| dq}
\]  

The mean group velocity corresponding to the whole \( i \)-th band is defined as \( <V> = \frac{(\alpha/\pi) \int_0^{\pi/\alpha} |\partial \omega_i/\partial q| dq}{d} \). The mean group velocities computed for each optical band are given in Table 7.1.

The frequency width of the wavepacket affects its group velocity (Eq. 6). Therefore, the group velocities were computed for each chain band for the frequency range corresponding to the 1/\( e \) peak width of the two stretching transitions initiating the wavepacket, \( \nu(\text{N}=\text{N}) \) and \( \nu(\text{N-C}) \), and the results are given in Figure 7.4A, inset and Table 7.1. The experimentally measured transport speed of 14.4 Å/ps is close to those calculated for the CH\(_2\) wagging (15.4 Å/ps) and twisting (11.2 Å/ps) bands. The group velocity supported by the CH\(_2\) rocking band is significantly larger than the experimental value. Small density of states in this band results in a low quality of the formed wavepacket and reduces its throughput. Thus we conclude that the CH\(_2\) twisting and wagging bands contribute most to the transport initiated by the \( \nu(\text{N}=\text{N}) \) mode.

Different from the \( \nu(\text{N}=\text{N}) \) mode relaxation, there are many decay pathways with comparable rates for the carbonyl stretching mode relaxation, both in the CH\(_{n}\)-a and CH\(_{n}\)-
s compounds (Figure 7.3B,C). Because of the presence of many relaxation channels for \( \nu(C=O) \) in CH\( n \)-a, the energy transport through the chain may occur via several chain bands. However, the similarity of the speeds in the CH\( n \)-a and CH\( n \)-s compounds (8.0 Å/ps) suggests that the same chain bands are most important for the transport in both cases. While the tag in CH\( n \)-a is located right at the chain end, the tag in CH\( n \)-s, \( \nu_{\text{as}}(C=O) \), is buried deep in the succinimide ester end group, and several IVR steps are required for the excess energy to reach the chain. By the time the excess energy in CH\( n \)-s reaches the chain, which is ca. 3 ps (Figure 7.2D),\(^5\) the mean energy for the succinimide ester modes bearing excess energy is expected to be much smaller than that in CH\( n \)-a after the first relaxation step, due to a much larger number of degrees of freedom at the succinimide ester moiety, compared to that at the carboxylic acid. Figure 7.4C shows the excess populations, compared to the thermal populations, for all modes below 1550 cm\(^{-1}\) for CH3-s. The overall excess population in the modes with frequencies above 730 cm\(^{-1}\), which is the cutoff for the optical bands of the chain, after 3 ps of relaxation is substantial at 0.53 (\( \Sigma \Delta n \)). To access those optical bands, the high-frequency modes at the ester site need to be used, as the ester spatially separates the end group from the chain. The highest frequency modes at the ester, except \( \nu(C=O) \), are associated with the N-O-C stretching motions (\( \nu_{\text{as}}(\text{NOC}) \) at 1083 cm\(^{-1}\) and \( \nu_{\text{ss}}(\text{NOC}) \) at 1052 cm\(^{-1}\)). The population excess in these modes remains substantial at 3 ps delay (Figure 7.4B). Due to spatial proximity to the chain and high frequencies, the N-O-C stretching modes are the most probable candidates for the doorways modes for the energy transport to the optical bands of the chain.

The high-frequency doorway states at the ester, \( \nu_{\text{ss}}(\text{NOC}) \) and \( \nu_{\text{as}}(\text{NOC}) \), frequency match two regions of the C-C stretching bands and one region of the CH\(_2\) rocking band
(Figure 7.4A, violet boxes). The $1/e$ width of the $v_{\text{as}}$(NOC) absorption peak centered at 1068 cm$^{-1}$ was experimentally determined to be 30 cm$^{-1}$ (Figure 7.1B). Assuming that the peak width of the $v_{\text{ss}}$(NOC) transition is similar, the range of frequencies of the end-group doorway modes was taken from 1035 to 1093 cm$^{-1}$ (Figure 7.4A, violet boxes). Dramatically different energy transport speeds are obtained for the three bands matching the doorway states: 66 and 7.6 Å/ps for the C-C stretching bands and 32.8 Å/ps for the rocking band (Figure 7.4A, Table 7.1). The speed of 7.6 Å/ps, supported by the C-C stretching band matches the experimental speed of 8.0 Å/ps, whereas the two other speeds do not. Note that the number of states of a band that are in resonance with the end-group states is inversely proportional to the group velocity; much higher transport efficiency is supported by the C-C stretching band featuring a small group velocity. The contribution to the $T_{\text{max}}$ values associated with the groups of states featuring much higher speeds is expected to be small because of the small density of states and a cross-peak contribution at small waiting times. Thus, the transport speed calculations suggest that the C-C stretching band contributes the most to the ballistic transport initiated by $v_{\text{as}}$(C=O) in the CH$n$-s compounds.

The local symmetry at the chain-ester link provides additional arguments for evaluating the contributions of the two bands in question: the C-C stretch and CH$_2$ rocking. With respect to the plane formed by the atoms of the ester (C-(C=O)-O-N) or the acid (C-(C=O)-O-H), the anti conformation for the nearest CH$_2$ group is the most stable with the dihedral angle $\theta$ of 180 degrees (Figure 7.5A). The atomic displacements associated with the two doorway states of the ester, $v$(NOC), occur in the ester plane. In the anti conformation ($\theta = 180^\circ$), the displacement of the two hydrogen atoms in the CH$_2$ rocking
modes, represented by the nearest CH$_2$ group, is perpendicular to the ester plane, resulting in a zero coupling of the ν(NOC) with the CH$_2$ rocking. However, the potential energy surface is shallow and a range of conformations along θ are thermally accessible at room temperature (Figure 7.5A). A mean coupling strength for the ν$_{as}$(NOC) with the two stretching modes and three rocking of the chain in the CH$_3$-s compound was evaluated as a function of the dihedral angle θ (Figure 7.5B, see SI). Clearly, the ν$_{as}$(NOC) mode is coupled much stronger to the stretching modes of the chain (Figure 7.5B). Taking into account the Boltzmann factor the graph 5C is obtained. Considering the Boltzmann factor (Figure 7.5C), the difference in the density of states (inversely proportional to the group velocity), and using the Fermi Golden rule, the 13-fold faster rate was obtained for the ν$_{as}$(NOC) mode decay into the C-C stretching vs. CH$_2$ rocking modes of the chain, confirming the importance of the former.
**Figure 7.5. A.** DFT computed potential energy surface for CH3-s along the C-C-C-O dihedral angle (θ), see inset. Mean square couplings strength of the ester stretching modes to the C-C stretching and CH$_2$ rocking states (B) and their values weighted by the Boltzmann factor (C). The ratio of the integrals under the curves in panel C equals 4.4; multiplication by the density of states ratio (~3) results in ca. 13-fold dominance of the relaxation rates into C-C stretching vs. CH$_2$ rocking modes of the chain.

An attempt to find similar doorway states in the CH$_n$-a compounds following v(C=O) relaxation were unsuccessful. The analysis of the relaxation channels of a range of CH$_5$-a compounds differing by their conformations, anti or gauche, at different carbon sites, showed the presence of a variety of decay channels which populate significantly the states below the 1300 cm$^{-1}$ frequency. The small zero-chain-length intercept in the $T_{\text{max}}$ vs. distance dependence of 0.95 ps (Figure 7.2C) suggests that the vibrational relaxation of v(C=O) in the CH$_n$-a compounds directly generates the wavepacket into the chain. The overall wavepacket formed this way consists of many states from different bands. However, the bands featuring small group velocity (and large density of states) will mostly contribute to the measured $T_{\text{max}}$ values. There are only two regions in the optical bands below 1300 cm$^{-1}$ where the group velocity is relatively small: those are the C-C stretching band around 1070 cm$^{-1}$ (Figure 7.4A, violet box) and the CH$_2$ rocking band around 730 cm$^{-1}$ (Table 7.1). The actual mean speed supported by the band depends on the frequency span (the bandwidth) of the wavepacket. Importantly, the speed comparable with that observed experimentally, is supported by both these bands.

It is unlikely that acoustic bands are transporting vibrational energy efficiently within the molecule as they are strongly coupled to the solvent.$^{38}$ They also have a much higher speed and low density of states; thus, the $T_{\text{max}}$ values are not expected to be sensitive to their contribution.
The tags discussed above, ν(N≡N), νₘₐₓ(C=O), and ν(C=O), have frequencies that are substantially higher (>230 cm⁻¹) than the frequencies of the closest chain band states, found at 1470 cm⁻¹ (Figure 7.3D & 7.4A). It is expected that if the tag frequency falls within a chain band, the wavepacket of this chain states can be initiated without additional anharmonically driven relaxation steps.⁴⁵,¹⁸² Such tag would allow selecting directly the chain band for the wavepacket transport.

To test this prediction, the N≡N stretching mode of the azido moiety (Figure 7.3E), which falls within the CH₂ wagging and CH₂ twisting chain bands (Table 7.1), was used as a tag with the νₘₐₓ(C=O) mode as a reporter. The waiting time dependences for the CHₙ-s series were measured. Different from the ν(N≡N) and ν(C=O) initiations, the cross peak amplitudes at early waiting times (T~200 fs) are already substantial for all compounds, indicating the existence of underlying weak succinimide ester transitions in the 1300 cm⁻¹ region with strong direct couplings to the νₘₐₓ(C=O) mode. Nevertheless, the infrared absorption in the 1300 cm⁻¹ region comes predominantly from the ν(N≡N) mode, as seen from the comparison of the spectra of the CH₅-s with the reference compound (CH₅-s-ref), where the azido moiety is replaced by a hydrogen atom (Figure 7.7); the spatial closeness between the underlying succinimide ester transitions and the reporter site permits their direct coupling. This statement is further confirmed by the observation of a cross peak at the same frequencies from the reference compound. The kinetic behavior of this cross peak was measured and used as a baseline for all the CHₙ-s measurements. The transport speed evaluated from the linear fit is 11 ± 4 Å/ps (Figure 7.6B).
Figure 7.6. A. Waiting time dependence of the $\nu(N=\text{N})/\nu_{\text{as}}(\text{C}=\text{O})$ cross-peak amplitude for the CH$n$-s compounds at ca. 45 mM concentration. The fit with a two-exponential function is shown (red). B. Dependence of $T_{\text{max}}$ vs. the tag-reporter distance measured for the CH$n$-s compounds for the energy transport initiated by the $\nu(N=\text{N})$ tag and recorded with the $\nu_{\text{as}}(\text{C}=\text{O})$ reporter. The linear fit (red) resulted in the transport speed of 11 ± 4 Å/ps.

The transport speed determined for the direct excitation on the $\nu(N=\text{N})$ mode matches the speed calculated for the CH$_2$ twisting and CH$_2$ wagging band regions overlapping with the $\nu(N=\text{N})$ spectrum, 15.4 and 11.2 Å/ps, respectively. It is also in agreement with the speed of 14.4 Å/ps measured for the transport initiated by the $\nu(N=\text{N})$ tag excitation, which was shown to be dominated by the pathway via the $\nu(N=\text{N})$ mode. Excitation of the $\nu(N=\text{N})$ mode with infrared pulses demonstrated that ballistic transport
can be initiated directly, opening the opportunity of controlling the transport speed by selecting specific chain bands for the wavepacket transport.

![Figure 7.7. Linear absorption spectra of the CH5-s (blue) and reference (CH5-s-ref, black) compounds in the fingerprint region, normalized for the ν(CO) mode, and the difference between them (red). The region corresponding to the ν(N=N) mode in CH5-s is shaded.](image)

7.4 Conclusions

To summarize, a combination of the experimental and theoretical studies permitted identifying the optical bands responsible for the ballistic transport in alkanes when initiated by four different tags. Different chain bands are found to be most important for different
cases of transport initiation, thus demonstrating different energy transport speeds. For the transport initiated by $\nu(N=N)$, we found that the CH$_2$ twisting and CH$_2$ wagging chain bands contribute the most to the energy transport. For the $\nu(C=O)$ initiation, the C-C stretching and CH$_2$ rocking chain bands were identified as the dominant energy transporter, both in the CH$n$-a and CH$n$-s compounds. In the case with the $\nu(N\equiv N)$ and $\nu(C=O)$ tags, the chain bands were far in energy from the tag and IVR relaxation steps were required to initiate the wavepacket in the chain. Direct excitation of the local mode, $\nu(N=\equiv N)$, which is coupled directly to the chain states resulted in the transport speed characteristic for the matching optical bands, CH$_2$ twisting and wagging. This study presents a consistent quantitative picture for describing the energy transport via alkane chains. Understanding the role different chain bands play in the energy transport will help in designing molecular systems with much higher energy transport speed and systems where the transport can be controlled.

7.5. Acknowledgment.

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The synthesis of the CHn-a and CHn-s compounds was performed by Hong Zhang, Boyu Zhang, and Xiao Zhou.
List of References


24. Busby, M.; Matousek, P.; Towrie, M.; Vlček, A., Ultrafast excited-state dynamics of photoisomerizing complexes fac-[Re(Cl)(CO)3(papy)2] and fac-


114. Grusenmeyer, T. Spectroscopic Investigation Of Intersystem Crossing, Electron Transfer, And Energy Transfer In Sn(iv), Re(i), And Ru(ii) Complexes In Solution. Tulane University, Tulane University, 2014.


130. To characterize the T1 state of the **Re3DMABN** compound, besides B3LYP, three other functionals, including cam-B3LYP, LC-wPBE, and wB97x, were adopted to study its CT nature. These functionals have been shown to have better performance in the description of CT states. All these functional predicted that the nature of the T1 state is LLCT, which does not agree with the experimental observation. Additionally, the shifts of the vibrational frequencies are also inconsistent with the experiments.


150. Rossenaar, B. D.; Hartl, F.; Stufkens, D. J., Reduction of Re(X)(CO)3(R'-DAB)]
(X = Otf-, Br-; DAB = Diazabutadiene; R' = iPr, pTol, pAn) and Re(R)(CO)3(iPr-DAB)]
(R = Me, Et, Bz) Complexes: A Comparative (Spectro)electrochemical Study at Variable

151. Delor, M.; Sazanovich, I. V.; Towrie, M.; Spall, S. J.; Keane, T.; Blake, A. J.;
Wilson, C.; Meijer, A. J.; Weinstein, J. A., Dynamics of ground and excited state
vibrational relaxation and energy transfer in transition metal carbonyls. *J. Phys. Chem. B*
**2014**, *118*, 11781-11791.

carbons": experimental studies of highly vibrationally excited molecules with stimulated

153. Pasupathy, A. N.; Park, J.; Chang, C.; Soldatov, A. V.; Lebedkin, S.; Bialczak, R.
C.; Grose, J. E.; Donev, L. A.; Sethna, J. P.; Ralph, D. C., et al., Vibration-assisted electron

154. Xiao, D.; Skourtis, S. S.; Rubtsov, I. V.; Beratan, D. N., Turning Charge Transfer
1818-1823.

155. Newton, M. D., Modeling donor/acceptor interactions: Combined roles of theory


157. Medvedev, E. S.; Stuchebrukhov, A. A., Inelastic tunneling in long-distance


174. Tesar, S. L.; Kasyanenko, V. M.; Rubtsov, I. V.; Rubtsov, G. I.; Burin, A. L.,
Theoretical study of internal vibrational relaxation and energy transport in polyatomic

175. Kurnosov, A. A.; Rubtsov, I. V.; Burin, A. L., Communication: fast transport and


177. Barone, V., Anharmonic vibrational properties by a fully automated second-order


179. Burin, A. L.; Tesar, S. L.; Kasyanenko, V. M.; Rubtsov, I. V.; Rubtsov, G. I.,
Semiclassical model for vibrational dynamics of polyatomic molecules: Investigation of

180. Lin, Z.; Bendiak, B.; Rubtsov, I. V., Discrimination between coupling networks of
glucopyranosides varying at a single stereocenter using two-dimensional vibrational

181. Tasumi, M.; Shimanouchi, T.; Miyazawa, T., Normal Vibrations and Force

182. Benderskii, V. A.; Kotkin, A. S.; Rubtsov, I. V.; Kats, E. I., Vibrational energy
transport in molecular wires JETP Letters 2013, 98, 219-222.