

Ultrafast spectroscopy of organic and hybrid semiconductors

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Declaration

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"People's Dreams... Have No Ends"

— Eiichiro Oda, One Piece

Abstract

The sensational discovery of conductive polymers in 1977 marked the start of a new field of science and technology – soft electronics. For this discovery the 2000 Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan MacDiarmid, and Hideki Shirakawa. Since then a range of exciting applications have been developed based on novel types of organic and hybrid materials including light-emitting diodes, solar cells, and field-effect transistors. These devices offer unique advantages over their classic inorganic counterparts, for example, being low cost, light-weight, flexible and easily chemically tunable. The development of new materials for high efficiency soft electronic devices requires detailed understanding of their intrinsic physics. It is well understood that fundamental physical processes controlling device performance, for example exciton formation and charge generation, are dynamic and fast in nature. The lifetimes of these processes are often at the femto- and nano- second timescales, which are not accessible by conventional spectroscopies. Fortunately, another fascinating field has emerged at the end of XX century – ultrafast spectroscopy, which makes possible probing the fast dynamics of electronic excitations in semiconductors by extremely short (from nano- to atto- seconds) pulses of light.

List of abbreviations

DFT	density functional theory
DSB	dynamic symmetry breaking
e-ph. interaction	electron-phonon interaction
FET	field-effect transistor
FTIR	fourier-transform infrared spectroscopy
HF	high frequency
HOIP	hybrid organic-inorganic perovskites
IR	infrared
IRF	instrument response function
IS	inorganic semiconductor
LED	light-emitting diode
LF	low frequency
MD	molecular dynamics
MHPs	metal halide perovskites
MIR	middle infrared
NIR	near infrared

OLED	organic light-emitting diode
OLET	organic light-emitting transistor
OPV	organic photovoltaics
OS	organic semiconductor
OSC	organic single crystal
PC	photocurrent
PL	photoluminescence
PV	photovoltaics
QM/MM	quantum mechanics/molecular mechanics modelling
SC	single crystal
SF	singlet fission
TAS	transient absorption spectroscopy
TRTS	time-resolved THz spectroscopy
VC	vibrational control
VIPER	vibrationally promoted electronic resonance spectroscopy
VIS	visible

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Motivation

The XX century was a true era of technological and scientific breakthroughs. Due to scientific discoveries, there has been significant improvement in the quality and longevity of human life. Many researchers and philosophers have associated this rapid improvement with the discovered new ways of harvesting and storing energy¹. Indeed, for centuries the main source of mechanical energy was simply provided by the labor of biological organisms, such as humans or domesticated animals. The discovery of new much more effective ways of harvesting, storing, and transferring energy has led to rapid industrialization and urban development around the world².

Technological modernization is still actively ongoing in the XXI century. However, to facilitate further progress, we need to overcome a major energetic crisis³. Each year, the global demand for energy continues to rise. However, we can no longer rely on non-renewable energy sources, such as coal, oil, and natural gas due to the major environmental issues. The complicated economic situation imposes other additional requirements for novel energy sources: significant increase in energy consumption is occurring in developing countries, which do not

always have easy access to fossil fuels, other useful minerals, and the most modern technological capabilities. Therefore, new energy sources must be easily accessible, cost-effective, eco-friendly, and safe⁴.

One of such energy sources is simply the energy of our star – solar energy. It is the most abundant energy source, accessible in every corner of the world. The energy of the sun can be clearly called renewable, as our star will remain in the present state for about 5-6 billion years⁵.

Sun has a fascinating physics behind its energy production. Essentially, the sun is a star fusion reactor in which protons fuse with each other to form helium atoms. During this process, a lot of energy is released in the form electromagnetic radiation that is emitted in all directions, subsequently reaching our planet as well⁵. The fusion reaction is one of the most effective known up to date in relation to the energy gained per unit mass of the expended substance. Therefore, it is not surprising that for more than 50 years a lot of efforts of the scientific community has been dedicated to developing a terrestrial thermonuclear reactor — more than 100 prototypes have been built, and it has been proven to be an exceptionally difficult problem⁶. However, if energy produced with the thermonuclear process is already surrounding us in the form of solar radiation. Why don't we harness solar energy first?

One of the best ways to harvest the energy of the sun is solar cell technology or photovoltaics (PV). PV has a huge number of advantages. It is environmentally friendly – producing very little greenhouse gases, abundant, easily accessible – requires very little infrastructure for operation, which makes it very attractive for developing countries, and very safe. Such significant advantages have led to a major increase in the share of photovoltaics in global energy production^{7,8}. However, the manufacturing of conventional solar cells often includes complicated and costly steps, for example, growing of high purity single crystals of silicon. This significantly increases the cost of solar panels and hinders the spread and development of PV technology⁹.

One of the most perspective ways to overcome this issue is the development of new PV technologies based on organic and hybrid semiconductors^{9,10}. Such materials are usually solution-processable, which means compatibility with inexpensive methods of PV materials deposition, such as “roll to roll”¹⁰. Furthermore, they have unseen before flexibility in terms of substrate for deposition, which implies they could be suitable for wider household applications (e.g. semi-transparent PV windows). Organic and hybrid materials have already revolutionized the field of LED and have been commercially successful¹¹.

This thesis is devoted to answering some of the unsolved questions in the physics of organic and hybrid photovoltaic materials. Part 1 gives an overview of the soft optoelectronics materials and relevant photophysics. Part 2 provides a detailed description of the experimental methods. Part 3 is devoted to ultrafast singlet fission dynamics in high quality organic single crystals of Rubrene. Part 4 is dedicated to role of organic cation in organohalide perovskite revealed by the photoluminescence (PL) and photocurrent (PC) Vibrationally Promoted Electronic Resonance (VIPER) spectroscopies. Part 5 is focused on PL VIPER spectroscopy study of Rubrene single crystals and its findings.

Part 1. Introduction

This chapter introduces the field of soft optoelectronics and the key condensed matter physics related to these fascinating materials. The first sub-chapter (I) is dedicated to the history of organic electronics development and the differences between organic and inorganic semiconductors. Sub-chapters (II) and (III) are devoted to reviewing the electron-phonon interaction and singlet fission phenomena in organic materials, providing the necessary background for the findings presented in Parts 3 and 5. Sub-chapter (IV) is a review of the recent emergence of a new class of hybrid semiconductors - metal-halide perovskites (MHPs). Their development, advantages, and some open questions of their optoelectronic properties are addressed in this sub-chapter. Finally, sub-chapter (V) is a general review of the material actively studied in this thesis: Rubrene single crystals. Rubrene is a benchmark semiconductor, which is well suited to study some of the fundamental processes of soft optoelectronics.

I. Soft semiconducting materials

1.1 History of organic electronics

Organic electronics has a 73-year history of development that is represented in the scheme below (Figure 1)¹².

The first discovery of semiconducting properties of materials comprised of organic molecules may be attributed to Akamatu and Inokuchi (1950)¹³. They have studied electrical conductivity of violanthrone, iso- violanthrone and pyranthrone powdered samples. In their experiments a small amount of the substance was placed in a cylinder with conductive ends serving as electrodes, and electrical current was measured between the ends of the cylinder as a function of pressure and temperature. They measured a weak (10^{-9} A) electrical current between the electrodes under the known applied voltage to measure the resistivity dependence on temperature and pressure. Remarkably, they found that the resistivity of the samples decreased with temperature under the constant pressure — a typical behaviour for semiconductors. The $\rho(T)$ dependence they identified allowed them to correctly estimate the activation energy as twice the bandgap of the studied substances. This study has correctly assigned

semiconducting properties to an organic material and can be referred as a first “foundation stone” of organic electronics.

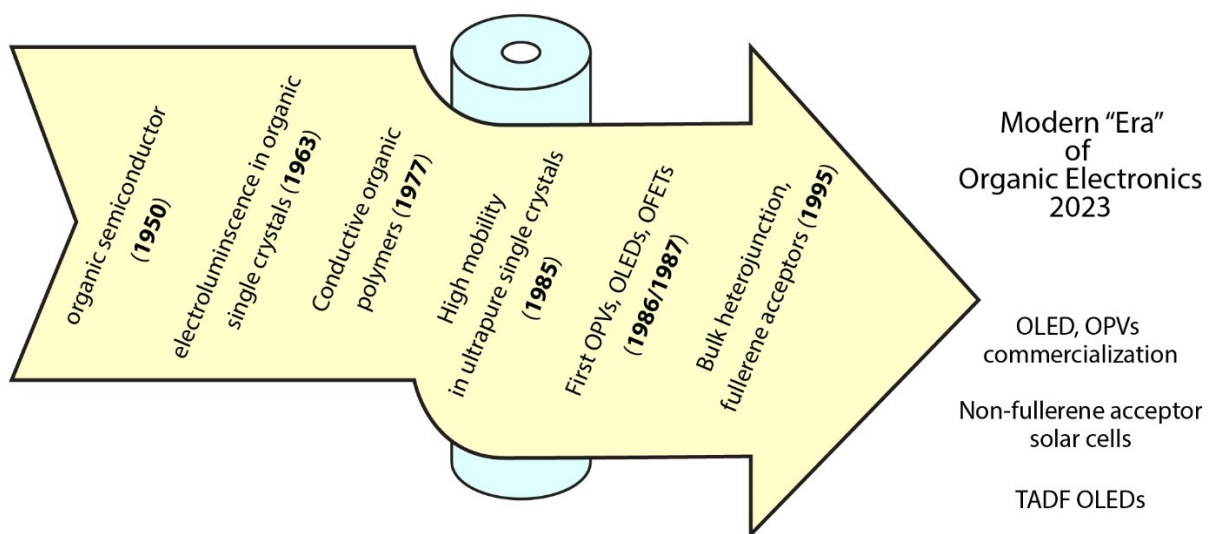


Figure 1. Key milestones in the development of organic electronics.

The next significant stage in the development of organic electronics can be assigned to the discovery of electroluminescence in organic single crystals. In these studies, researchers demonstrated luminescence in single crystals of anthracene upon injecting charges at high voltages ($>100\text{V}$) via aqueous electrodes¹⁴. These proof of principle studies demonstrated a new phenomenon for organic electronics that would eventually be employed in light-emitting

devices such as organic light-emitting diodes (OLEDs). Though the first demonstration of OLED would be done only 20 years later by Tang et al¹⁵.

Since the middle of the 20th century, doping has been a very well-known way of controlling electrical properties of inorganic semiconductors. For example, doping silicon with arsenic atoms turns it into n-type semiconductor with increased concentration of electrons and, hence, conductivity. Sensationally, similar possibility was discovered for organic polymers in 1977 by Alan J. Heeger, Alan MacDiarmid, and Hideki Shirakawa^{16,17}. In their works, they doped an insulating polymer *trans*-polyacetylene with arsenic pentafluoride (AsF₅) and achieved a sevenfold increase in conductivity! They showed that upon substantial doping, an intrinsically insulating polymer can be even turned into a conductor. This discovery has revealed high potential of organic materials for the next generation of electronics and marked a starting point for the new field of science and technology – soft electronics. The discovery made by Heeger, MacDiarmid and Shirakawa has earned them the 2000 Nobel Prize in Chemistry.

After this point, the emergence of real functional devices was only a matter of time. Therefore, further developments of organic electronics is related to practical implementation of organic electronics devices. The first OFET was demonstrated by Tsumura et al. in 1986¹⁸. They used gold electrodes and polythiophene organic

polymer as a semiconductor. Authors reported charge carrier mobility of $\sim 10^{-5}$ cm^2/Vs and find electrical characteristics similar to those in metal-oxide-semiconductor (MOS) FETs.

The first bi-layer OPV cell and OLED were reported by a Kodak group in 1985 and 1987 respectively^{15,19}. The OPV cell comprised of layers of copper phthalocyanine and a perylene tetracarboxylic derivative. For that time this innovative bi-layer design allowed to achieve impressive 1% power conversion efficiency (PCE). The OLED was another major step forward. For the first time, organic electroluminescent device with quite good efficiency (1%), high brightness ($> 1000 \text{ cd/m}^2$) was achieved with low operating voltage ($< 10\text{V}$).

The last device innovation that should be mentioned is the invention of the bulk heterojunction (BHJ) solar cell in 1995^{20,21}. Increased efficiency of bi-layer OPV cells have demonstrated the importance of the organic/organic interface in the active layer of the device. In bi-layer OPV cells, however, once excitons are generated in donor (D) and acceptor (A), they should diffuse over a considerable distance to reach the D/A interface to subsequently generate charges. Hence, excitation geminate recombination (exciton annihilates with another exciton) was found to be a dominating loss channel during this diffusion process. To mitigate these recombination losses, the BHJ strategy was suggested. In BHJ solar cell, two

components are finely mixed into bi-continuous interpenetrating network that creates a large surface area for excitons dissociation at the D/A junction. The large interface surface area and interpenetrating morphology minimizes the distance that excitons have to diffuse to dissociate, therefore, minimizing recombination losses. This approach, with the standard implementation of polymer-donor/fullerene-acceptor, has allowed to achieve 11.7% PCE for single-junction solar cells and 7-9% PCE for modules²². The BHJ strategy has undoubtedly defined the direction of organic solar cells development for many subsequent years, and it is still a standard approach today for the OPV device engineering. Among the disadvantages can be noted low ambient stability of BHJ blends^{23,24}.

Last but not least, I would like to note the enormous role played by theoretical research in the development of organic electronics. Fluorescent resonant energy transfer (FRET) developed by Förster^{25,26}, despite initially being developed for photosynthetic complexes, is now widely applied to describe energy transport in organic electronics systems and beyond. FRET (also often referred as Förster) is a radiative process based on dipole-dipole interaction of two emitters and occurs at distances of a few nanometers. At shorter distances, another mechanism, similar to tunnelling, takes place. Described by Dexter in 1953 it is known as *exchange energy transfer* (often referred as Dexter) mechanism²⁷. Another important

transfer mechanism was developed by Marcus²⁸, who won the Nobel Prize in Chemistry in 1992 for his seminal contributions. *Marcus electron transfer* is used to describe the hopping charge transfer mechanism characteristic of low mobility ($<1\text{cm}^2/\text{Vs}$) organic semiconductors. A rational development of the Marcus theory is the *Holstein theory*, which additionally considers the formation of a polaron — a quasiparticle that takes into account the interaction of a hole or an electron with the environment^{29,30}.

FRET, EET, Marcus and Holstein theories are classics of organic semiconductor physics, but by no means exhaustive for exciton and charge transfer in organics. These theories provide a good basis for understanding transfer processes in many organic materials and are often used as a foundation for more complicated modelling.

Organic electronics started its journey over 70 years ago. During this period, the field has gone from the initial observation of electroluminescence to the successful commercialization of OLEDs — their wide use in TVs and smartphone displays¹². Organic electronics has also begun to reserve its place in the solar panel industry: thanks to the much-improved PCE^{31,32}, in recent years, we have seen an unprecedented number of startups adopting organic semiconductors as a go to material for solar cells. The majority of startups are yet to achieve financial

success; however, it can be clearly said that the OPV technology has begun to commercialize³³.

Despite wide and successful commercialization, it would be wrong to assume that there are no more or even less scientific interest in the field. Conversely, organic electronic systems have become more complicated and require more sophisticated modelling and experimental techniques to create new types of devices, even further improve efficiencies and understand new phenomena. For example, new technological advances has allowed development of new types of organic electronic devices: organic light-emitting transistors (OLETs)^{34,35} — a device that combines functions of both a transistor and an OLED, and highly sensitive sensors based on self-assembled organic monolayers³⁶. Among the current hot fundamental research topics, I would like to highlight (1) complicated photophysics of charge carrier generation in novel non-fullerene acceptor solar cells³⁷, (2) the role of intermolecular vibrations in high mobility organic semiconductors³⁸, (3) exciton dynamics in thermally activated delayed fluorescence OLEDs³⁹, (4) singlet fission mechanisms and dynamics⁴⁰.

Ultrafast spectroscopy plays an important role in studying abovementioned phenomena, primarily due to its well-established ability to capture the dynamic nature of these processes with exceptional temporal resolution^{37,41,42}.

1.2 Difference of organic and inorganic semiconductors

When Akamatu and Inokuchi¹³ wrote on the first evidence of semiconducting properties in organic matter, they suggested that this type of semiconductors should be called “intrinsic”, because of the unclear conductance mechanism without the obvious presence of impurities. Indeed, where does the semiconducting properties of organic matter come from?

Inorganic semiconductors

In inorganic semiconductors, such properties originate from the energetic structure of the material as well as from the doping with other atoms^{12,43,44}. Covalently bonded atoms (Figure 2, a) result in the formation of bands.

Figure 2b gives an example of a typical band energetic structure of an inorganic semiconductor (e.g. silicon) with the valence and conduction bands. These bands are separated from each other by an energy gap or **bandgap**, where there are no eigenstates. In an intrinsic semiconductor, the fermi level is located between the conduction and valence bands, hence, at 0K, electrons populate states in the valence band and there are no electrons in the conduction band. However, at room temperature (RT, 300K), some of the electrons are getting thermally promoted to the conduction band.

In the conduction band, the electrons (same applicable for holes) move almost freely within a semiconductor body due to a substantial level of delocalization¹². This also results in a quite high levels of mobility at 100-10000 cm²/Vs at RT among most of inorganic semiconductors⁴⁵.

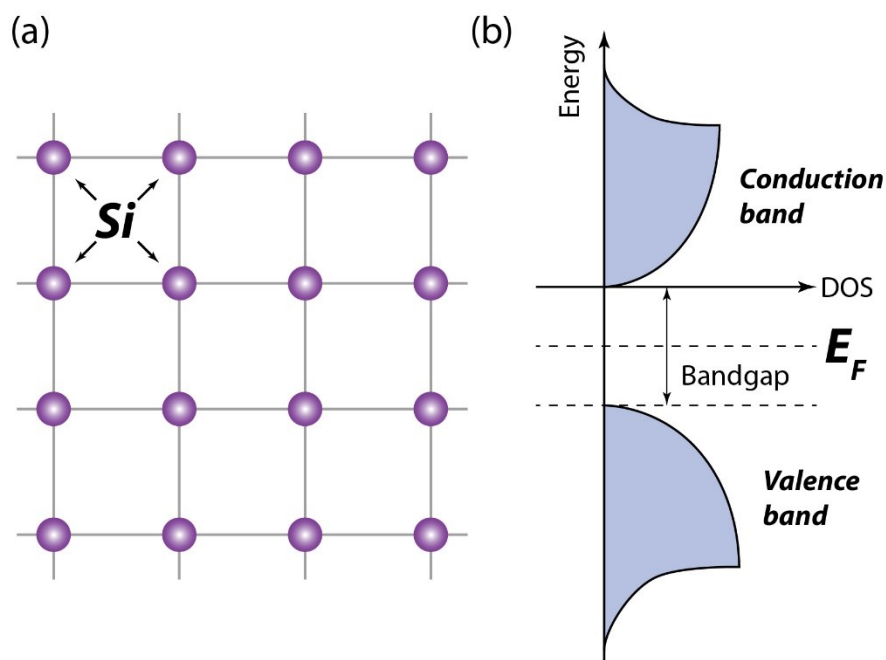


Figure 2. Schematic of the silicon (Si) crystal structure. (a) Covalently bonded atoms are formed into a rigid structure. (b) Schematic of the energetic structure of a typical inorganic semiconductor. Here DOS is the density of electronic states. E_F is the fermi energy.

Electrons in the nearly empty conduction band respond well to an applied electric field. However, for practical applications the level of conductivity in

pristine semiconductors is often not enough. To increase the conductance and tune the conductivity type (switch between p- or n- types) the doping method is typically used^{12,43,44}. For this, some of the atoms within a semiconductor are replaced with the atoms of other elements, which can donate or withdraw electrons. Energetically, this means adding some extra occupied states nearby the conduction band (to donate electrons, Figure 3, a) or valence band (to withdraw electrons and donate holes, Figure 3, b). The energy levels of these states should be close enough to the bands, so electrons or holes of the doping element could be thermally activated to the corresponding bands⁴³.

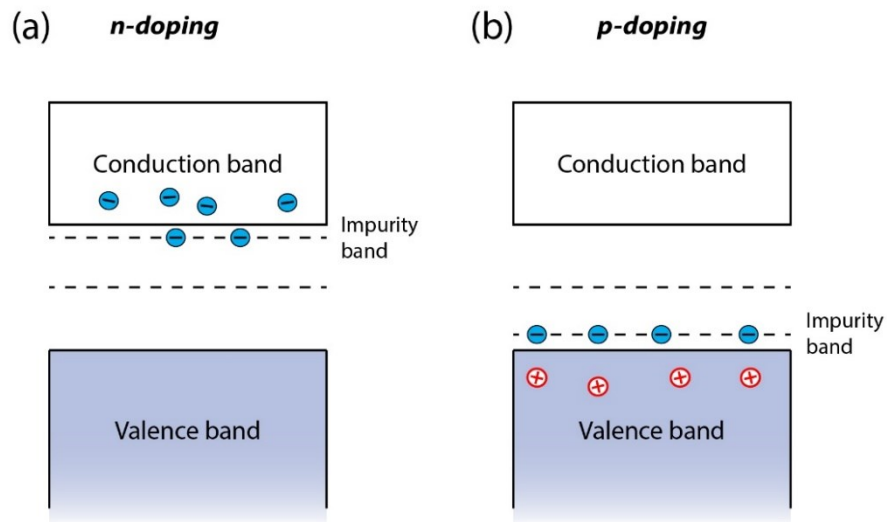


Figure 3. Energetic schemes of n-type doping (a) and p-type doping (b).

Doping can be illustrated well using the example of the most popular and famous semiconductor — silicon. To dope this material a small amount of impurity is added to the crystal structure, for example n-type dopant arsenic (**As**) (Figure 4, a)⁴³.

Arsenic has 5 valence electrons, while silicon has only 4. Therefore, once an As atom is incorporated into the Si crystal structure, four As electrons bond to Si atoms, but the fifth electron remains unbonded. Energetically, this means that there is no room for the fifth electron in the valence band, hence it should go to the conduction band, move “freely”, and contribute to the conductance.

However, the As atom without its fifth electron has a net positive charge that should bind the donated electron and form another exciton-like state. But, because of the high concentration of highly mobile carriers in inorganic semiconductors, there is a very effective electrostatic screening of the positively charged **As** atoms¹². Due to such screening, the binding energy of the fifth electron and As ion is extremely small (about 0.02 eV), which make this bond to be easily broken at room temperature (300K, 0.025 eV) with temperature-induced fluctuations¹². Therefore, as we anticipated the fifth electron goes to the conduction band, becomes mobile and contribute to the conductance!

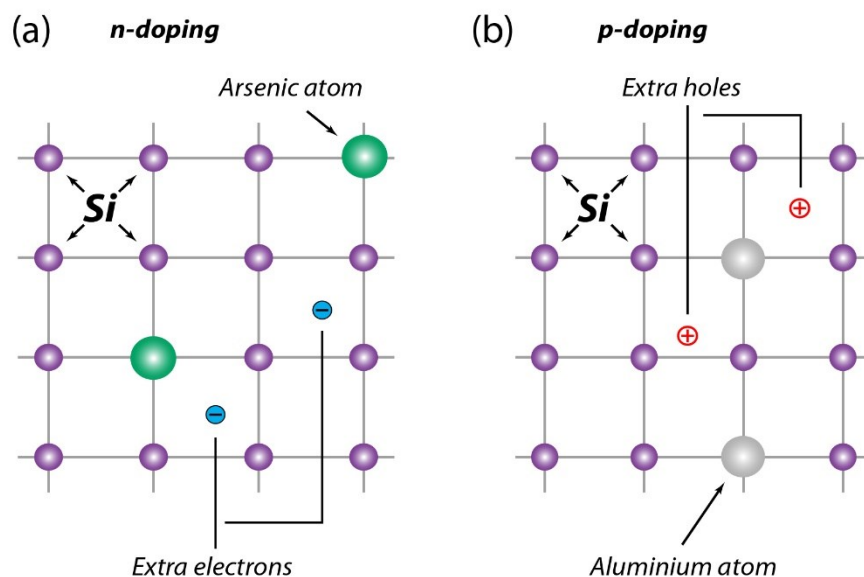


Figure 4. Doping: the example of silicon. N-type doping with arsenic atoms (a). P-type doping with Aluminium atoms (b).

The abovementioned scenario, in which extra electrons are donated into the semiconductor and contribute to the conductance is called n-type doping. The same can be achieved to induce a p-type conductance in a semiconductor. In *Si*, for example, this is often done with introducing electron-withdrawing (hole donating) atoms of aluminium (Figure 4, b)⁴³.

Organic semiconductors

As we have seen above, semiconducting properties of inorganics, such as band formation and doping, are defined by high levels of **electronic delocalization**¹². But

how about organic semiconductors? In organics, semiconducting properties originate from the formation of π -orbitals, π -orbitals overlap and wave functions delocalization along them^{12,46–49}.

Let us consider the formation of **π -orbitals** on the example of a simple ethylene molecule (Figure 5, a). This molecule comprises of 2 carbon atoms bonded with a double bond and 4 hydrogen atoms.

It is well known that carbon has a valence of two without hybridization and a valence of four if hybridization is taking place⁴⁷. In the case of ethylene, sp^2 type of hybridization is taking place, which means that one 2s orbital hybridizes with two 2p orbitals resulting in three sp^2 orbitals. Figure 5 shows energy levels (b) and orbitals (c) for electrons of a non-hybridized carbon and a hybridized one.

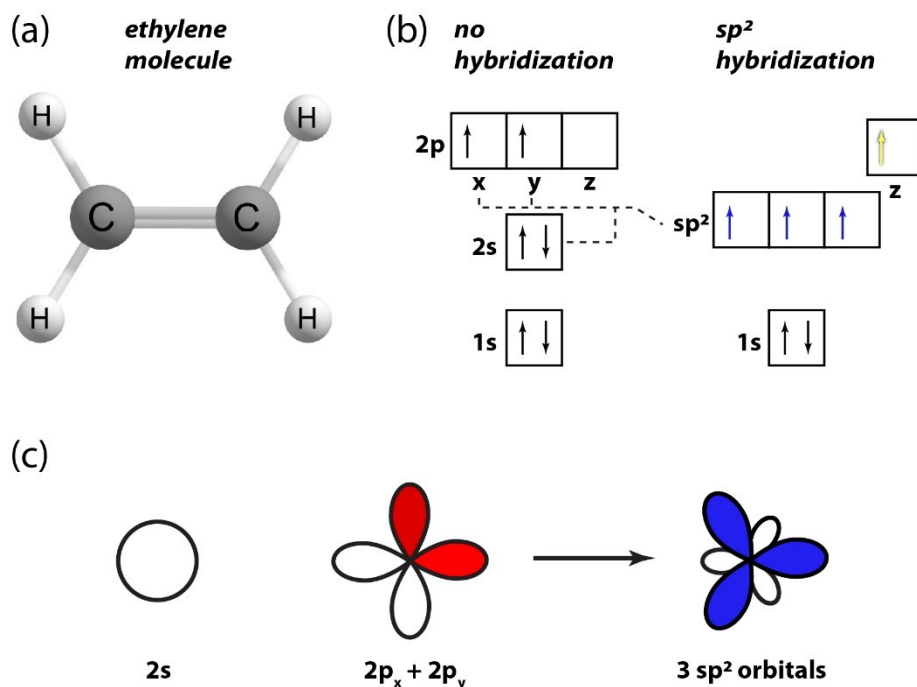


Figure 5. Ethylene molecule (a) and sp^2 orbitals hybridization (b, c). Energy and orbital filling scheme (b). Orbitals wavefunctions shape with and without hybridization (c).

Once carbon atoms are brought together to form a molecule, the individual wave functions of the electrons overlap and, by the Pauli exclusion principle, can no longer be in the same quantum state, which splits the original energy levels into two new different levels (Figure 6, a)^{12,46}.

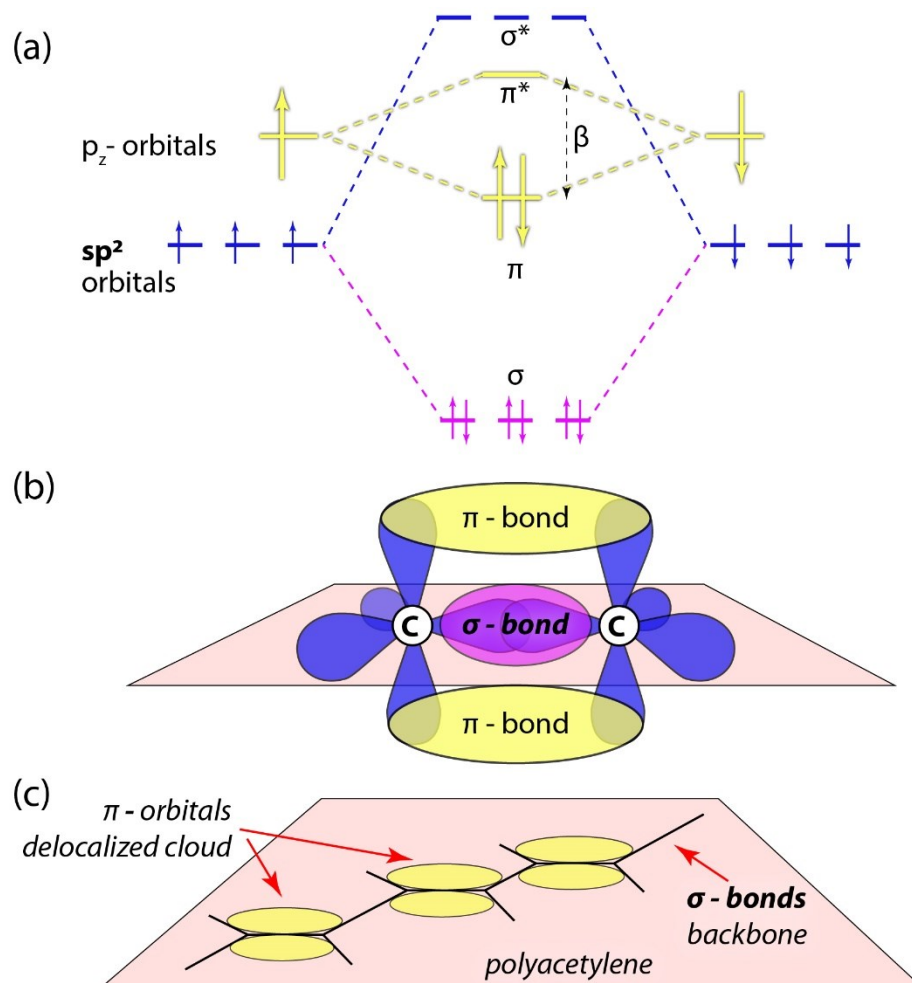


Figure 6. π - and σ - orbitals formation in organic semiconductors. (a) The energy levels of two carbon atoms form the energy levels of an ethylene molecule. (b) Diagram of the wavefunctions in the ethylene molecule. (c) Schematic of the polyacetylene organic polymer: σ - orbitals form an in-plane backbone, π - orbitals form a delocalized electron cloud defining semiconducting properties of polyacetylene.

Hence, sp^2 and $2p_z$ energy levels are split and new orbitals are formed to chemically bond the carbons. Sp^2 levels are split into σ and σ^* , $2p_z$ energy levels are split into π and π^* . Because π^* and σ^* have larger energies, they are not involved in the covalent bonds formation. The first bond between carbon atoms (C-C) is due to the overlapping sp^2 hybridized orbitals and is called sigma (σ) bond. The second C-C bond is formed by the overlapping $2p_z$ orbitals and is called pi (π) bond. As can be seen in the Figure 6(a), there is an energy gap between the last populated orbital π (highest occupied molecular orbital — HOMO) and the subsequent unpopulated orbital π^* (lowest unoccupied molecular orbital — LUMO). This energy gap is analogous to the bandgap in inorganic semiconductors, and the magnitude of this energy splitting can be calculated, for example, using the Hückel model ^{46,50–54}(Appendix A):

$$E_{\pi/\pi^*} = \alpha \mp \beta, \quad (I. 1)$$

$$\beta = H_{12} = H_{21}; \alpha = H_{11} = H_{22}, \quad (I. 2)$$

$$H_{ij} = \langle \varphi_i | \hat{H} | \varphi_j \rangle, \quad (I. 3)$$

where $\hat{H}$ is a Hamiltonian and $|\varphi_{i,j}\rangle$ are $2p_z$ carbon atomic orbitals.

Before moving forward, we should also note that there are two additional sp^2 hybridized orbitals remained unbonded for each of the carbon atoms remaining

(as there are $2 \times 3 = 6$ sp^2 orbitals in total and only 2 are used to form the C-C σ bond). In the ethylene molecule, these orbitals are forming sigma bonds with 1s orbitals of hydrogen atoms.

We now address the shapes of the wavefunctions of the formed π and σ orbitals, as well as the physical differences between them. Corresponding new orbitals for both σ and π bonds are shown in the Figure 6b. Essentially, σ orbitals form a backbone (in-plane for ethylene) for the molecule, whereas π orbitals form a delocalized electron cloud above^{12,48,49}. This observation for the simple molecule of ethylene may be expended for the whole range of organic semiconductor molecules made up of many more carbon atoms (with addition of hydrogens, of course, and other functional elements).

In more complex organic materials, such as polymers and organic single crystals, π - orbitals induced delocalization can be much more significant than 2 carbon atoms observed in ethylene. For example, If several sp^2 -hybridized carbon atoms are bonded in a row, then each 2p orbital overlaps with a pair of neighboring ones (sometimes even with three), and therefore the corresponding electron (π -electron) cannot be assigned to any one bond. This effect is called **conjugation (or π -conjugation)**, and the corresponding electrons are called **conjugated**^{12,47–49}. Figure 6c demonstrates this effect on the example of a simplest

semiconducting polymer (polyacetylene): an in-plane σ -bonded framework is formed by sp^2 hybridized orbitals, while p electrons are delocalized in a framework of π -bonds.

Conjugation defines the main properties of organic semiconductors. The substantial level of delocalization allows charge transfer to occur when external electric field is applied, although not as effective as in inorganic counterparts¹². Additionally, π -electron system introduces lower values of redox potentials (potentials required for oxidation or reduction of the materials) compared to sigma-bonded molecules⁴⁸. This allows easy 'doping' by charge transfer from electron-withdrawing or donating species, such as iodine¹⁶, oxygen, or calcium⁵⁵.

Therefore, both doping and charge transport become possible in organic materials. However, there are significant differences compared to their inorganic counterparts, which can be well illustrated with the help of an organic single crystal (OSC) energy level structure.

Differences of organic and inorganic semiconductors

Single crystals are the most efficient class of organic semiconductors with the best charge transfer properties^{12,56}. A single crystal consists of a large number of molecules having sp^2 -hybridized carbon atoms and 2p electrons. Thus, for each

molecule many π - orbitals are formed (shown in Figure 7, a). Unlike inorganic semiconductors, the molecules are not connected to each other by covalent bonds. Instead, weak van der Waals bonds of an electrostatic nature are formed between the molecules^{12,34}. As the molecules come closer, the π -orbitals overlap, and the energy levels split even more.

This leads to the energy structure shown in Figure 7b. Similar to the ethylene molecule, HOMO and LUMO energy levels (and orbitals) are formed with the energy gap separating them. However, there are many more energy levels, because there are more electrons in the system! Energy levels below HOMO are populated, whilst levels above LUMO are unpopulated.

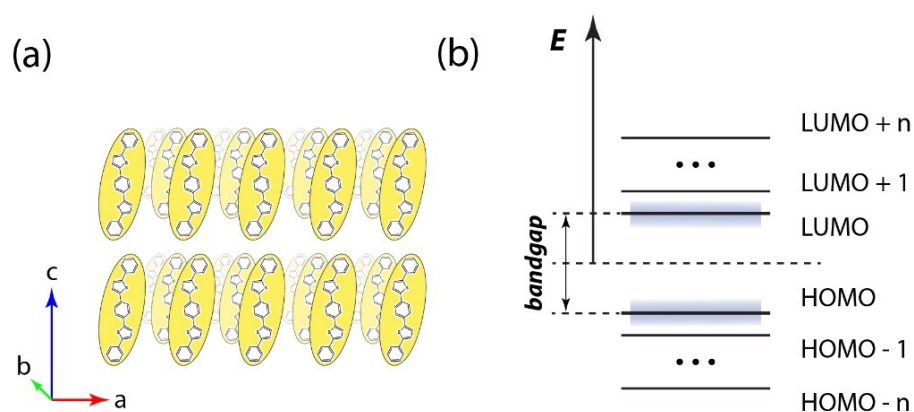


Figure 7. Structural and energetic structure of an organic single crystal. (a) Structural schematic: molecules are tightly packed within the single crystal with the π -orbitals of adjacent molecules overlapping with each other. (b) Energy levels

in a molecular crystal. Grey areas around HOMO and LUMO indicate the formation of narrow bands in the single crystal.

As can be seen in Figure 7b, in OSCs there is no continuous density of states, which is observed for inorganic counterparts (Figure 2, b). Deeper orbitals in OSCs (down to HOMO-n/ up to LUMO+n) are relatively independent of each other, because of the weak interactions between “buried” electrons of adjacent molecules¹². However, if there were no interactions between orbitals of adjacent molecules at all, charge transfer in organic semiconductors would be impossible! Therefore, there must be some sort of intermolecular orbital interaction, which in fact is observed for the delocalized π -orbitals. Essentially, π -orbitals of adjacent molecules overlap with each other, and hence corresponding electrons may delocalize even more (can be over several molecules). Therefore, the conjugation effect⁴⁸, which has been previously described for the case of the simplest molecules and linear polymers, is expanded for the case of the solid-state organic materials.

From the energetic perspective, this is schematically depicted in the Figure 7b via appearance of very narrow energy bands shown with colour gradients around HOMO/LUMO energy levels. Quantitatively, in the best-case scenario of most tightly packed OSCs, the widths of such bands can reach ~ 500 meV¹².

The neighboring molecules in OSCs (and organic semiconductors in general) are interacting via the weak van der Waals forces. Because of this, such materials are often referred as **soft** in the literature⁵⁷. The softness not only determines the energy structure, but also affects nearly all other properties of organic semiconductors. Below, we will list the particularly important ones.

1. **Charge transfer.** As have been highlighted above, charge transfer in organic semiconductors is far less effective than in inorganic counterparts^{12,58}. For the best case of Rubrene single crystals, the values of charge carrier mobility can reach only about $20 \text{ cm}^2/\text{Vs}$ ^{56,59}, which is orders of magnitude lower than for the inorganic crystalline semiconductors: $\mu_e = 1450 \text{ cm}^2/\text{Vs}$, $\mu_h = 370 \text{ cm}^2/\text{Vs}$ for Silicon; $\mu_h = 400 \text{ cm}^2/\text{Vs}$, $\mu_e = 9000 \text{ cm}^2/\text{Vs}$ for GaAs⁴⁵. The reason for smaller mobilities in organic materials is hugely affected by the impact of molecular vibration on the orbital overlap and charge delocalization. Such a phenomenon is called **electron-phonon interaction**³⁸ and will be described in detail in one of the subsequent sub-chapters.
2. **Flexibility.** This is one of the main advantages of organic semiconducting materials. Because of the weak interactions of molecules, organic

materials can be easily stretched, bent, and folded without compromising electronic properties and mechanical integrity⁶⁰.

3. **Processibility.** This is another important advantage of organic semiconductors over the inorganic counterparts. In contrast with the challenging growth requirements of conventional semiconductors, films of soft semiconductors (major part) are readily deposited on a variety of materials at room temperature. This makes this class of materials to be uniquely suitable for large area applications, such as displays and solar cells^{12,61}.
4. **Excitons.** The soft structure of organic semiconductors also results in a significant binding energy of electrons and holes. A photon absorption in an organic semiconductor result in formation of an exciton⁶², which is a bound state of an electron and a hole attracted to each other via the electrostatic Coulomb force. Excitons are also formed in inorganic semiconductors, but their binding energy is typically extremely small ($\ll kT$), hence they easily dissociate to free carriers via temperature activation^{12,63}. The stronger exciton binding energy in organic semiconductors is also related to the small dielectric constant (2-3) compared to the inorganic counterparts (10-15)^{12,64,65}.

5. **Polaron formation.** There are still significant differences in physics of organic and inorganic semiconductors even after dissociation of excitons into electrons and holes. Since there is no significant concentration of free charge carriers for screening (as in inorganics), in organics the charges polarize the surroundings material and deform it, creating a kind of self-induced trap¹². This state of the deformed lattice and charge is called a **polaron**. The formation of polarons in organic semiconductors is one of the factors that hinders charge carriers' delocalization^{66,67}.

Those are the main differences of organic and inorganic semiconductors, which are consequential of the soft nature of organic semiconducting materials. There are of course many more differences not highlighted here, for example, in the technological perspective of growing single crystals, depositing films, etc. For this, we would like to refer the reader to the literature, for example in [68] and [69].

Last, it would be important to highlight one crucial advantage of organic semiconductors — **tunability**.

Tunability simply means exceptional opportunities for adjusting properties by modifying the chemical structure of organic compounds⁷⁰. This is associated with the extensive capabilities of modern organic chemistry, which allows for the

modification of molecules and polymer chains - the structural units of organic materials – with very little limitations. Therefore, fluorescent⁷¹, transport⁷², mechanical, and other properties important for electronics can be easily customized when such a need exists. This is a truly unique advantage of organic electronics, which allows designing materials to meet specific requirements of the desired application. Combined with the softness and processibility, this allows designing multi-layered structures with new unique properties different from the properties of the individual layers¹². This unveils new possibilities for device architectures that are beyond the reach of traditional inorganic semiconductors.

II. Electron-phonon interaction

Due to the soft structure of organic materials, molecular vibrations have a significant influence on the semiconducting properties of organic semiconductors. This phenomenon of vibrations affecting the electronic properties of materials is referred to as electron-phonon (e-ph.) interaction^{38,58,73}. Here the main focus will be on the influence of e-ph. interaction on the charge transport process and mobility of organic semiconductors. As such, it is suggested that this context be borne in mind when this section is being perused. We shall begin this part by examining the fundamental terms and definitions.

2.1 Terms and Definitions

Intermolecular and intramolecular vibrations

It is relatively easy to find a number of distinctive vibrations (normal modes) in any organic molecule. This number can be found as $3N-5$ for linear molecules and as $3N-6$ for non-linear ones, where N is the number of atoms comprising the molecule⁷⁴ (in the solid state there are $3N-3$ optical modes, 3 acoustic modes; N is the number of atoms per unit cell). However, how different these vibrations from each other and do they affect charge transfer in the same manner?

There are two types of e-ph. interaction in organic semiconductors. The first one is referred to as **local** (Holstein) and is associated with the intramolecular vibrations, which are localized on the individual molecules. Such vibrations are typically high frequency with the wavenumbers above 200 cm^{-1} (usually above 1000 cm^{-1})^{38,58}. An example of such a vibration is given in Figure 8a. As can be seen it only comprises of atoms moving at a specific molecule without involving any adjacent molecules. The local component is normally associated with the modulation of molecular energy levels and can be quantified using the reorganization energy (see below)³⁸.

The second type is called **non-local** (Peierls) e-ph. interaction^{38,58,73,75,76}. It is associated with vibrations that are disrupting charge delocalization over several molecular sites⁷³. Molecular vibrations associated with the non-local e-ph. interaction should have a certain degree of non-locality and expand over several molecular sites. This is normally associated with intermolecular vibrations, which involve moving atoms of adjacent molecules relatively to each other (Figure 8, b). Generally, in organic single crystals intermolecular vibrations have lower frequency ($<200\text{ cm}^{-1}$)⁵⁸. They are thermally populated at room temperature ($200\text{ cm}^{-1} \approx 25\text{ meV} \approx 300\text{ K}$), hence have large amplitudes (in classical terms) and provide significant fluctuations of the intermolecular distances³⁸. They are different

ways to characterize the non-local e-ph. interaction, but normally it is quantified with the modulation of charge transfer integrals via vibrational displacement — $\partial J/\partial Q$ (see below) or the lattice distortion energy³⁸ — L .

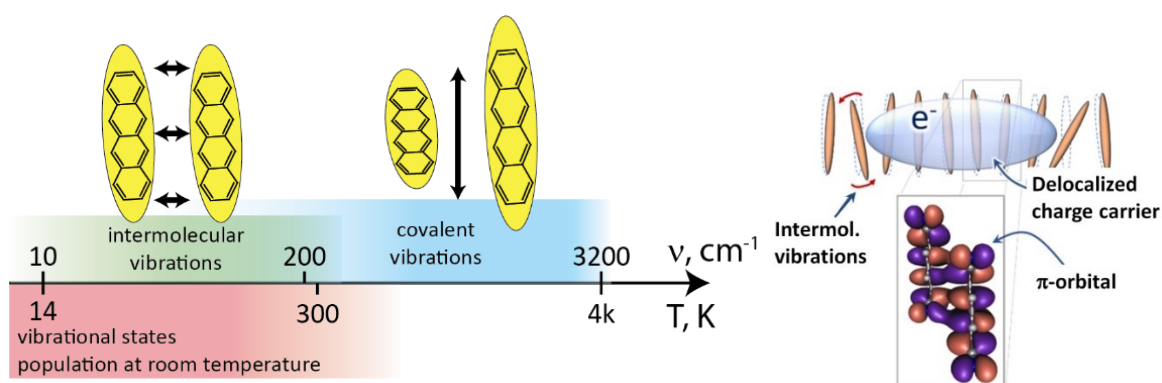


Figure 8. (a) Inter- and intramolecular vibrations in organic semiconductors: schematics, frequency range, and thermal population at the room temperature. (b) The delocalization of charge carriers within an ordered lattice of small-molecule organic semiconductors is affected by low-frequency thermal molecular motion, which tends to disrupt this delocalization.

The 200 cm^{-1} wavenumber borderline should only be considered as a general guide and not be confused with a criterion of any kind that allows judging about inter- or intramolecular nature of the particular vibration. In fact, vibrations with energies below 200 cm^{-1} may be partially intramolecular for molecules with the soft core.

Reorganization energy

The **reorganization energy** concept⁷⁷ is used in many models of charge and energy transfer of organic semiconductors. It is used to evaluate local e-ph. interaction associated with the vibrational modulation of molecular levels. It is defined as the energy spend on changing molecular geometry during the transfer from one molecule to another.

The physical meaning of the reorganization energy is shown in the Figure 9 for the charge transfer process of the type⁷⁸:



, where charge moves from the molecule of the donor (D) to the molecule of acceptor (A). This process may be split into two steps. During the first step, the molecule of donor (D) is oxidized to an ion state and simultaneously the molecule of acceptor (A) is reduced to the neutral state ("1" in the Figure 9) at frozen reactant geometries. In the second step both charged donor (D^+) and reduced acceptor (A) are vibrationally relaxed to the corresponding optimal geometries ("2" in the Figure 9).

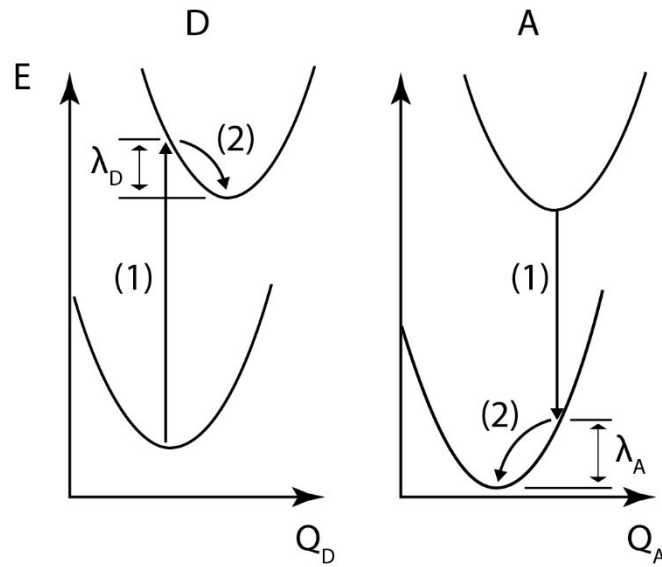


Figure 9. Reorganization energy definition for the charge transport from the donor (D) to acceptor (A). First step (1): oxidization of donor and reduction of acceptor. Second step (2): vibrational relaxation to optimal geometries.

Therefore, the reorganization energy is comprised of two contributions:

$$\lambda_{reorg} = \lambda^D + \lambda^A \quad (1.5)$$

, where λ^D is the contribution from the donor and λ^A is the contribution from the acceptor. For energy transfer, the reorganization energy is defined in a similar way using excited molecular states instead of the charged states. There is another contribution to the reorganization energy related to the polarization/relaxation of

the surrounding medium, which is referred to as the “outer contribution”. For this, we refer the reader to the detailed review [78].

Charge transfer integrals and on-site energies

The **charge transfer integral** is another important parameter that is necessary for the further consideration of transport in organic semiconductors (OS). It allows us to assess the degree of intermolecular delocalization of wave functions in OS. A charge transfer integral between adjacent molecules n - and m - may be simply defined as^{12,79}:

$$J_{nm} = \langle \phi_n(\mathbf{r} - \mathbf{R}_n) | H_e | \phi_m(\mathbf{r} - \mathbf{R}_m) \rangle \quad (I. 6)$$

, where J_{nm} is the charge transfer integral, $\mathbf{R}_n$ is the vector indicating the position of the n - molecular site, H_e is the charge transfer Hamiltonian. The non-zero value of J_{nm} is indicative of electronic coupling between the n - and m - molecular sites, allowing the existence of the delocalized states and their movement through the system⁷⁶.

If $n=m$, then the (I. 6) formula is transformed into the expression for the local on-site energy:

$$\varepsilon_{nn} = \langle \phi_n(\mathbf{r} - \mathbf{R}_n) | H_e | \phi_n(\mathbf{r} - \mathbf{R}_n) \rangle \quad (I. 7)$$

, where ε_{nn} is the expected energy value at the n- molecular site.

2.2 Electron-phonon interaction and charge transport

To describe the charge transfer process from one molecular site to another, we will use the following single electron Hamiltonian^{12,79}:

$$H_T = H_e^0 + H_{ph}^0 + H_e^{tr} + H_{e-ph}^{loc} + H_{e-ph}^{non} \quad (I. 8)$$

, where H_T is the charge transfer Hamiltonian factorized into several contributions.

The first two terms are given for the initial electron (H_e^0) and phonon (H_{ph}^0) population of the system. The electron population may be written as:

$$H_e^0 = \sum_n^N E_n^0 a_n^\dagger a_n \quad (I. 9)$$

, where E_n^0 is the energy of an electron at n-th site, $a_n^\dagger$ and a_n are electron creation and annihilation operators (for the mathematical properties see Appendix B), N is the total number of electrons in the system. Similarly, for the population of phonons:

$$H_{ph}^0 = \sum_{\mathbf{q},j} \hbar \omega_{\mathbf{q},j} \left(b_{\mathbf{q},j}^\dagger b_{\mathbf{q},j} + \frac{1}{2} \right) \quad (I. 10)$$

, where $\omega_{\mathbf{q},j}$ is the frequency of the phonon mode with the wavevector $\mathbf{q}$ at the j -th phonon branch; $b_{\mathbf{q},j}^\dagger$ and $b_{\mathbf{q},j}$ are phonon creation and annihilation operators.

Now with the system populated with electrons and vibrations, it is time to introduce charge transfer from one molecular site to another. For this we also can simply use the formalism of creation and annihilation operators:

$$H_e^{tr} = \sum_{m \neq n}^N J_{nm} a_n^\dagger a_m \quad (I. 11)$$

, where J_{nm} is the charge transfer integral between molecular site m -/ n -defined earlier. The physical meaning of (I. 11) is absolutely clear at first glance. In a nutshell, we are populating the n -th molecular site and depopulating m -th molecular site with the probability proportional to the $|J_{nm}|^2$.

The residual terms in charge transfer Hamiltonian (I. 8) are adding interaction between electronic and vibrational subsystems, i.e. electron-phonon interaction.

The **local** (intramolecular) contribution may be expressed as:

$$H_{e-ph}^{loc} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},j} \sum_m^N \hbar \omega_{\mathbf{q},j} (g_m(\mathbf{q},j) b_{\mathbf{q},j} + g_m^*(\mathbf{q},j) b_{-\mathbf{q},j}^\dagger) a_m^\dagger a_m \quad (l. 12).$$

, where the factors $g_m(\mathbf{q},j)$ and $g_m^*(\mathbf{q},j)$ are expressing strength of the coupling for the vibration with the wavevector $\mathbf{q}$ at the j -th phonon branch.

Similarly, the **non-local** (intermolecular) component is expressed as:

$$H_{e-ph}^{non} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},j} \sum_{\substack{m,n \\ m \neq n}}^N \hbar \omega_{\mathbf{q},j} (g_{nm}(\mathbf{q},j) b_{\mathbf{q},j} + g_{nm}^*(\mathbf{q},j) b_{-\mathbf{q},j}^\dagger) a_n^\dagger a_m \quad (l. 13)$$

, where $g_{nm}(\mathbf{q},j)$ and $g_{nm}^*(\mathbf{q},j)$ are expressing strength of the non-local coupling. Further we may refer to g_m (g_m^*) and g_{nm} (g_{nm}^*) simply as **local** and **non-local couplings** for conciseness.

Essentially, (l. 12) and (l. 13) are adding energetic *disorder* to the system related to molecular vibrations. Clearly, there is a resemblance between (l. 12) and (l. 13) — these formulas can be rewritten as one. Indeed, when describing e-ph. interaction, it is possible to combine the g_m and g_{nm} factors into a single matrix. In this case, the elements of local couplings will be located on the matrix's diagonal, while the elements of non-local couplings will be off the diagonal.

Therefore, in many theoretical studies local e-ph. interaction give rise to diagonal disorder, whilst non-local to off-diagonal dynamic disorder¹².

Equations (I. 8) – (I. 13) provide us with the necessary theoretical framework for solving problems and calculating charge transfer properties of organic semiconductors. An analytical solution for the full H_T Hamiltonian does not exist: it is solved numerically with the approximations and methods adjusted for a particular problem. These complex computational methods (such as MD and DFT) go far beyond the scope of this introduction^{38,73}. However, a lot can be understood about the charge transfer in organic semiconductors even from the structure and terms of H_T .

Before going deeper, we would like to note that the H_T (I. 8) is written for the case of transport in an ideally structured system of molecular sites, which very well corresponds to the case of high quality organic single crystals. In amorphous films, the crucial factor will be the energetic disorder caused by static disorder – defects. For this, an additional term(s) may be added to Hamiltonian (I. 8), accounting for static disorder, which will dominate the disordered systems¹².

There are several implications can be made considering the local and non-local e-ph. Interaction terms (l. 12) and (l. 13). When coupling constants are much bigger than transfer integrals¹²:

$$|g_{nm}|, |g_m| > J_{nm} \quad (l. 14)$$

,this would lead to the charge transfer dominated by polarons (hopping). This is caused by the charges being localized by the molecular vibrations on one molecular site, therefore, gaining significant effective mass.

On the contrary, if the opposite takes place¹²:

$$|g_{nm}|, |g_m| < J_{nm} \quad (l. 15)$$

, the polaronic effects will be small, charges tend to delocalize, and the transport becomes “band-like”. In most inorganic semiconductors, electron coupling is much stronger than electron-phonon interaction ($J \gg g$), which leads to full-fledged band transport. Band-like transport, in which electron is delocalized over several molecular sites, can be observed in organic single crystals at low temperatures⁸⁰.

In conclusion, it is vital to highlight the connection of coupling constants introduced in equations (14) and (15) and the more physically intuitive parameters for characterizing local and non-local electron-phonon interaction, which were initially introduced – the reorganization energy and transfer integrals.

It is possible to derive the following expression relating couplings $g_m(\mathbf{q}, j)$ with contributions to the reorganization energy and nuclear coordinate displacements³⁸:

$$|g_m(\mathbf{q}, j)|^2 = \frac{2M_j\omega_{\mathbf{q},j}}{\hbar} |\Delta Q_m(j)|^2 = \frac{\lambda_{\mathbf{q},j}}{\hbar\omega_{\mathbf{q},j}} \quad (l. 16)$$

,where $\lambda_{\mathbf{q},j}$ is the contribution to reorganization energy, M_j is the molecular mass, $\Delta Q_m(j)$ is the relative nuclear coordinate shift due to the corresponding molecular vibration (Figure 9).

Similar relation may be derived for the non-local couplings $g_{nm}(\mathbf{q}, j)$ ⁷⁵:

$$|g_{nm}(\mathbf{q}, j)|^2 = \frac{1}{2M_j\hbar\omega_{\mathbf{q},j}^3} \left(\frac{\partial J_{nm}}{\partial Q_m(j)} \right)^2 = \frac{L_{nm}(\mathbf{q}, j)}{\hbar\omega_{\mathbf{q},j}} \quad (l. 17)$$

,where L_{nm} are the contributions of various modes to the lattice distortion energy in the direction nm .

2.3 Vibronic coupling of electronic states

Another important phenomenon related to e-ph. interaction in organic semiconductors is vibronic coupling of electronic states^{81–83}. In this phenomenon, coupling of the two (or more) excited states is facilitated due to the molecular vibrations in the system. This may increase the energy/charge transfer rate from one excited (bright) state to the coupled one⁸², as well as lead to the formation of new delocalized eigenstates with the mixed electron–vibrational character^{82,84}.

Vibronic coupling for two excited electronic states is demonstrated schematically in the Figure 10. In this figure, we can see two cases for the interaction of the excited states: with the weak (a) and strong (b) vibronic coupling^{82,85}.

In the weak coupling regime (Figure 10, a), two overlapping excited states X and Y are energetically close enough for the excitation to transfer from the optically excited state X (bright state) to Y (can be dark state) via some sort of incoherent “hopping” process (see Part 1, Sections 1.1 and 2.2). Additional energy is required for this $X \rightarrow Y$ transition, which is typically borrowed from thermal fluctuations making this process temperature-activated.

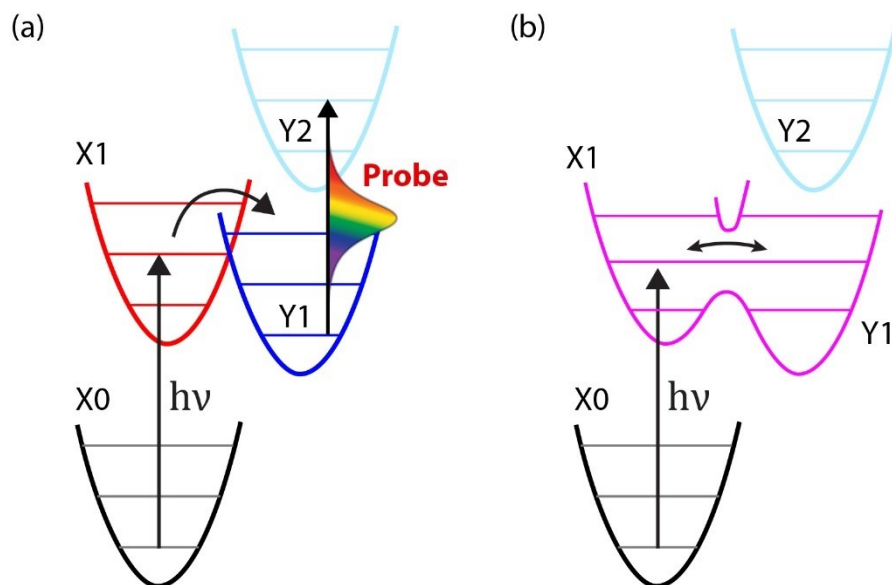


Figure 10. Schematic of vibronic coupling of two electronic states. (a) Case of the weak coupling. Transfer from the states X to Y is incoherent. (b) Case of the strong coupling. States X and Y become sufficiently mixed that may facilitate coherent energy transfer. For both cases, the emergence of the states may be monitored with ultrafast spectroscopy techniques, for example, transient absorption (see Part 2, Section I) or two-dimensional optical spectroscopy⁸².

The weak vibronic coupling regime can be recognized with various spectroscopic techniques. For example, it can be pinned down with ultrafast spectroscopic techniques. For example, it can be pinned down with ultrafast transient absorption (TAS, see Part 2, Section I). In TAS experiment, the bright state X is initially photoexcited by a short optical “pump” pulse (“ $h\nu$ ” in the Figure 10, a). The resulting optical excitations are then monitored using another short “probe” pulse (Figure 10, a). In this experiment, we observe how the absorption

of the “probe” pulse changes depending on its delay from the “pump” pulse. Therefore, in the case of weak vibronic coupling, it would result in immediate appearance of the peaks associated with the X state (and ground state bleach), and then after some time delay (typically tens of picoseconds) the appearance of the peaks associated with the Y state.

In the strong coupling regime (Figure 10, b), both states $|X\rangle$ and $|Y\rangle$ are coupled to a vibrational mode with a similar frequency. In this regime, there is an avoided crossing along the vibrational coordinate at which the potential energy surfaces of X and Y would cross. The strong mixing of electronic and vibrational wavefunctions makes possible generation of the mixed delocalized eigenstates⁸² $|XY\rangle$.

Strong coupling regime can be similarly recognized with several ultrafast spectroscopy techniques. In particular, it can also be identified with the ultrafast TAS technique (see Part 2, Section I). In this scenario as both states are strongly vibronically mixed with each other, one may expect to observe both features of $|X\rangle$ and $|Y\rangle$ in the TAS signal appearing after the photoexcitation.

Vibronic coupling is often discussed as a prospective method for improving the power conversion efficiencies of solar cells. For instance, it is well-established that the efficiencies of organic photovoltaic (OPV) devices are limited by short exciton

diffusion lengths, attributed to an ineffective 'hopping' mechanism of exciton transport. In this context, the coherent mechanism (in this case, coherence is associated with spatial coherence, i.e., the phase correlation of the wavefunction amplitudes of spatially distant states) of energy transfer, achievable in the active layers of devices when molecules are strongly vibronically coupled (Figure 10, b), is considered superior to the dominant hopping mechanism. If achieved, this coherent mechanism of energy transfer could facilitate the development of much more efficient OPV devices⁸².

III. Photo-excitation of organic semiconductors

This part of the introduction is dedicated to the light-matter interaction processes in organic semiconductors, electronic excitation, and their evolution within the materials. First, the general case of photon absorption is introduced in which excitons, coupled states of electrons and holes, are excited within semiconductors. Further, the spin-associated evolution of the states is considered. Special attention is paid to the process of *singlet fission* in which one singlet exciton is split into two triplet excitons⁷⁰. The physics of the latter phenomenon has recently attracted major attention within the OPV scientific community due to this process of having high potential for improving efficiency of PV devices⁸⁶. The Part 3 of this thesis is devoted to disentangling the complicated physics of singlet fission via ultrafast transient absorption using ultrapure single crystals of Rubrene as a model system.

3.1 General case

Photon absorption

Due to the huge variety of organic semiconductors, photoexcitation process may vary quite significantly depending on material composition, morphology, and

chemical structure¹². Here, we will consider the simplest case of light absorption of a single organic molecule. This model, however, is essential, as the more complicated cases, such as absorption of single crystals, films and even blends of organic molecules can be built upon this model.

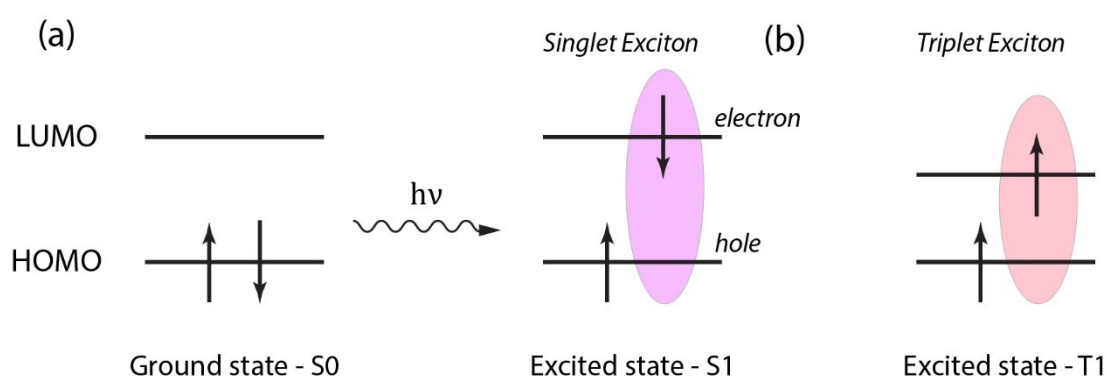


Figure 11. Light absorption via a single organic molecule. Arrows indicate spin directions of electrons that populate energy levels. Only HOMO and LUMO levels are shown for clarity since only electrons at these levels are involved in the excitation. (a) Singlet exciton excitation. (b) Triplet exciton schematics.

Figure 11a is reminiscent of energetic structure of an organic molecule¹². In ground state the levels below and including HOMO are populated, whilst the levels above and including LUMO are unpopulated. As a photon of light is absorbed with the energy equal or more to E_g (Figure 11, a), an electron from HOMO level is transferred to LUMO level, leaving a vacant place (hole) behind. Both the electron and the hole are attracted to each other via electrostatic forces; therefore, an

exciton is being excited. The total spin of the system in ground state and in the excited state is equal to zero, and the multiplicity of the states is therefore equal to 1 ($3J + 1$). Hence in such a case this transition is referred as $S0 \rightarrow S1$.

There are also triplet states (Figure 11, b), but their excitation does not occur directly due to the quantum mechanical prohibition^{12,48}. Further, we will also consider the pathways of triplet states formation.

Let us now consider the process of photon absorption in more details from the point of view of quantum mechanics. The transition rate between initial state (i) and final state (f) can be approximated by Fermi's Golden Rule^{87,88}:

$$k = \frac{2\pi}{\hbar} |\langle \psi_i | H_{int} | \psi_f \rangle|^2 \rho(E_{if}) \quad (l. 18)$$

, where $\psi_{i,f}$ are the wavefunction of the initial and final states, H_{int} is the interaction Hamiltonian, and $\rho(E_{if})$ is the joint density of states of the initial and final wavefunctions.

In the first order of approximation, the interaction Hamiltonian is given by the electric dipole transition⁸⁹:

$$H_{int} = -\vec{\mu}\vec{E} \quad (I. 19)$$

, where $\vec{\mu}$ is the dipole moment operator and $\vec{E}$ is the electric field.

Equations (I. 18) and (I. 19) together with Born-Oppenheimer approximation allows derivation of the quantum-mechanical selection rules for the optical transitions between the states:

1. Dipole transitions are allowed only between electronic states of the opposite spatial symmetry.
2. Transitions are only allowed between the same vibronic levels in two different electronic states. (When there is a substantial shift in molecular coordinates between E_i and E_f , this selection rule is broken).
3. Transitions are allowed only between the states with the same spin-multiplicity (for example: $S1 \rightarrow S2$; $T1 \rightarrow T2$).

Development of excitonic states

After light absorption, excited species in organic semiconductors (OS) (normally singlet excitons — $S1$) can follow various development pathways. Below, the main processes are introduced (Figure 12).

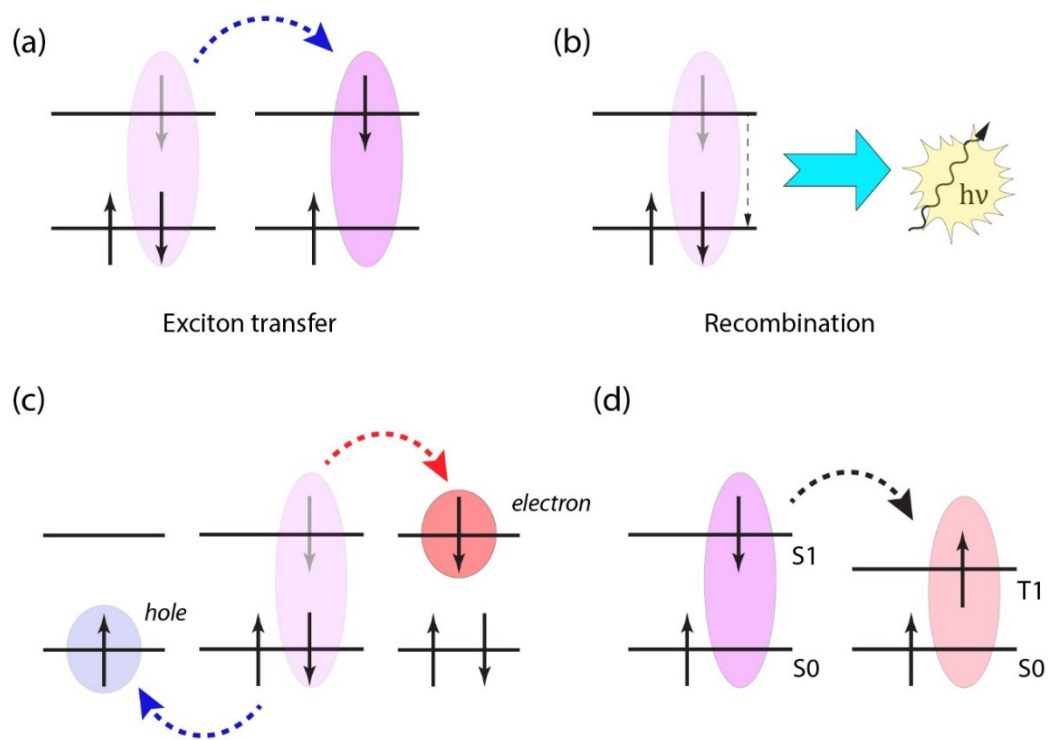


Figure 12. Electronic processes in organic semiconductors: (a) exciton transfer, (b) direct recombination, (c) dissociation, (d) conversion to a triplet exciton. More transparent arrows and oval areas represent past states before the processes in (a), (b) and (c) takes place.

Though, It is crucial to keep in mind that in real systems these processes likely to occur simultaneously with different intensity and probability. Often, these electronic excitations are dependent on each other and occur in both (forward and reverse) directions, which creates a complicated dynamics of the electronic evolution within OSs^{37,90}. Therefore, to gain insight into the full photophysical

picture of a particular OS, a set of time-resolved experimental techniques, such as transient absorption (see Part 2, Section I) or time-correlated single photon counting, must be used in conjunction with a kinetic model or numerical simulation (for example density functional theory or DFT). There is a huge variety of OSs, so the approach to each specific material is often individual. Considering this, we shall proceed to review the development of electronic processes.

1. Because excitons in OSs have quite significant binding energy ($\gg kT$), they can simply migrate to the neighbouring molecules (Figure 12, a) (if such neighboring molecules exist). This process is referred to as exciton transfer (diffusion) and the diffusion length (L_d) can reach several dozens of nm in OSs. The typical diffusion lengths L_d are 5-20nm for singlet excitons and 30-300nm for triplet excitons⁹¹. However, we shall note that values exceeding 100nm for singlets and 1 μm have been reported in several papers^{92,93}.
2. Secondly, electrons and holes can simply radiatively recombine (Figure 12, b). This process can occur with excitons localized either on one molecule or two or more adjacent molecules. In both cases, the electron(s) and hole(s) disappear, emitting photon(s) of light.

3. The electron and hole can also dissociate (Figure 12, c), separating from each other, leading to the formation of free carriers. Very often, this process can occur through intermediate states, known as Charge Transfer (CT) states³⁷.
4. Finally, there are processes involving spin conversion. The most common and major in OS is, of course, conversion of the singlet excitons to triplet excitons (Figure 12, d). The triplet exciton has a total spin value of one, therefore the multiplicity is equal to 3 ($3J + 1$), hence the name comes from this fact. The triplets excitons are normally lower in energy, however direct excitation of the triplet states is not possible due to the quantum mechanical prohibition. Normally, there is only a small probability of the singlet exciton to become the triplet state via the process called intersystem crossing (ISC)⁷⁰. Because the ground state of the typical organic molecule is singlet, the inverse transition back to the ground state ($T1 \rightarrow S0$) is forbidden as well. Because of this, triplets live in an organic semiconductor for an incredibly long time (typically microseconds, but can live up to seconds in exceptional cases⁹⁴ until $T1 \rightarrow S0$ transition occurs via phosphorescence or non-radiatively⁹⁵).

Triplets accumulation and lifetime of the triplet states are the questions that intrigued researchers for decades. Indeed, great efforts have been directed towards the use of organic molecules as the gain medium for lasing⁹⁶. In this case, the accumulation of long-lived triplet states over time is a harmful parasitic process that interrupts lasing. In the past, this problem was solved by using a liquid (solution) of organic molecules continuously pumped through the laser cavity so that triplets did not have time to accumulate. Overcoming this issue for solid state organic medium is essential for developing the next generation of organic current-injection lasers. There is currently active research aimed at finding a solution to the problem of triplet accumulation in organics⁹⁷.

However, can the triplets be being used for good? Recently, a way to use triplet states to improve the performance of solar photovoltaic cells has been proposed. This method is based on a phenomenon called singlet fission.

3.2 Singlet fission

Singlet fission is the more efficient and faster way to form triplets in OS. This is a process that results in the fission of one singlet exciton into two triplet excitons.

Recently, this phenomenon has attracted a lot of attention in the organic electronics scientific community⁷⁰.

The main requirement for the singlet fission to occur is the low enough level of triplet energy levels (T1) compared to the singlet levels (S1)⁹⁸. Intuitively, this means that the T1 energy should be at least as low, as the half of the S1 energy ($E_{T1} \leq E_{S1}/2$). However, this condition is normally not that strict, due to the possibility of temperature-activation and other nuances. The energetic threshold could be therefore formulated as:

$$E_{T1} \approx E_{S1}/2 \quad (I. 20)$$

The energetic requirement (I. 20) and efficiency of SF can be well demonstrated by the series of acene single crystals — from anthracene to pentacene (Figure 13). Anthracene has the T1 level much higher than the half of the S1 ($E_{T1} \gg E_{S1}/2$). Therefore, the SF process does not occur, and the majority of the excited states undergo direct recombination back to the ground state S0 with emission of photons (fluorescence). Still, some of the triplets would be formed via the intersystem crossing, but their portion under CW illumination may be considered negligible.

Further, when an additional annealed ring is added to the system, the relative position of the triplet energy level becomes low enough that condition (I. 20) is fulfilled, and the SF process is allowed. This is the case of tetracene, and it was shown to have SF⁹⁹.

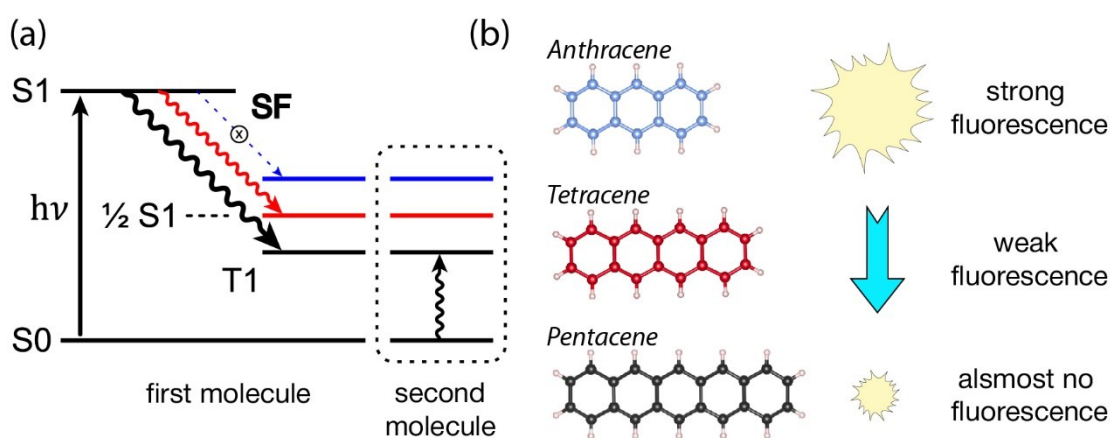


Figure 13. (a) Relative position of triplet energies compared to singlet energies in the series of acenes. Energies are normalized by S_1 level. (b) Corresponding to energy levels acenes molecules. Triplet levels are colour coded i.e., blue molecule corresponds to blue T_1 level, etc. (c) Corresponding change in fluorescence.

The photophysics of tetracene is affected by SF in a major way. The rate of triplet formation in tetracene via SF is much higher than in anthracene via ISC. Because of this, direct exciton recombination ($S_1 \rightarrow S_0$) is competed by triplet formation ($S_1 \rightarrow 2 \times T_1$), which significantly weakens the fluorescence.

This effect is even stronger in pentacene single crystals¹⁰⁰. In pentacene, the triplet energy level is lower and SF process is even more efficient. In fact, the rate of singlets to triplets conversion is so fast (~300fs) that the direct exciton recombination channel ($S_1 \rightarrow S_0$) is practically eclipsed by triplet formation ($S_1 \rightarrow 2 \times T_1$), and the fluorescence is almost completely quenched.

This example demonstrates the effectiveness of the SF process. At first glance, it would appear that SF is entirely determined by the relative positions of the S1 and T1 energy levels. However, this is not quite true⁹⁸. The physics of the singlet fission process is quite complex and is currently being actively discussed in the literature. For example, the role of the intermediate state for the singlet fission process is still actively debated⁷⁰:



, where X is an intermediate state. It is assumed that the X state may be a pair of coherently coupled triplet states (TT) (also known as multiexciton states). The role of such intermediates and the exact mechanism of formation is still under the debate. There are several mechanisms suggested. One of the suggestions is that there might be the direct coupling between the S1 and TT states. Another suggestion is that the CT (charge transfer) states might play a role. All the

mechanisms has been studied extensively via theoretical methods, however, there is a real challenge in testing these theories in experiments due to experimental limitations. Part 3 of this work is devoted to this problem.

Application example

Singlet fission was proposed to be used for improving efficiency of PV devices — not only organic, but also hybrid⁴⁰. Below, the suggested improving mechanism is described⁸⁶.

There are different types of energy losses in PV devices¹². One of the fundamental loss channels is thermalization (Figure 14, a). If the energy of the absorbed photon is $h\nu \gg Eg$, then the excess energy of hot excitons will be lost due to the relaxation. This is one of the factors limiting the efficiency of an ideal single junction silicon solar cell - the Shockley-Queisser limit, calculated at 29%.

Singlet fission can help to reduce these losses. For this a wide gap SF material must be combined with a standard small bandgap semiconductor (Figure 14, b). It would be ideal, if:

$$E_g(SF) = 2 \times E_g(SBM) \quad (I. 22)$$

, where $E_g(SF)$ is the bandgap of SF material and $E_g(SBM)$ is the bandgap of small bandgap semiconductor (material). If the SBM material is combined with a wide-gap SF semiconductor, then:

1. High-energy photons are absorbed by the SF material and converted into two triplet excitons for each photon with almost no thermalization losses!
2. Low-energy photons are transmitted through the SF material (below bandgap) and absorbed by the SBM; excitons are generated within SBM.
3. Triplet excitons are diffused to the SBM in which they are separated into charge carriers.

This tandem mechanism is designed to reduce thermalization losses. According to calculations, in an ideal silicon-SF PV device the efficiency can reach 35%, exceeding the Shockley-Queiser limit⁸⁶.

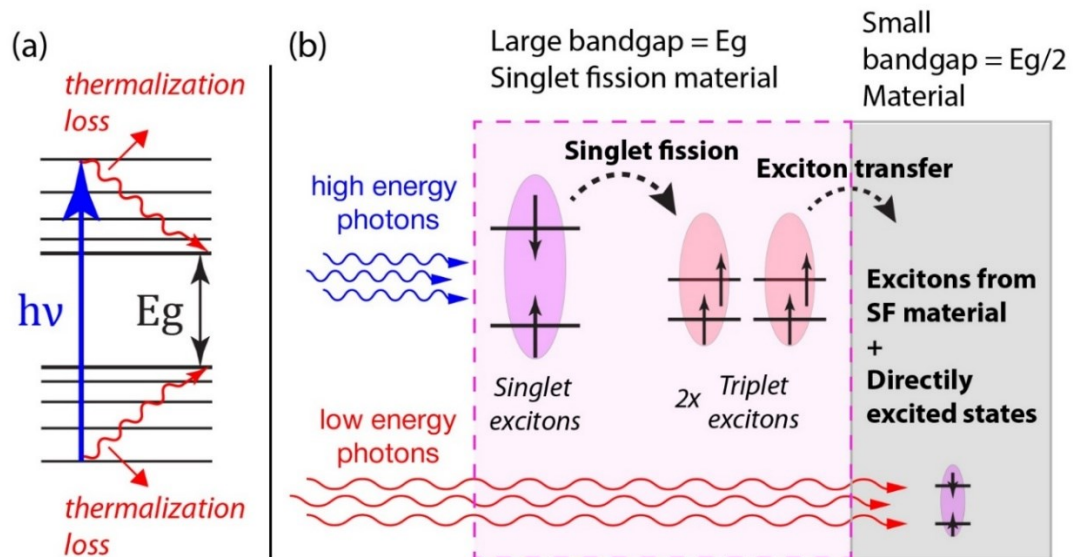


Figure 14. (a) Origin of thermalization losses in PV devices — excess photon energy is lost due to hot exciton cooling. (b) Tandem schematic for reducing thermalization losses in PV devices using SF material.

IV. Metal-halide perovskites

In section 1.2 of this work, we established the difference between organic and inorganic semiconductors (OSs and ISs). The advantages of OSs are low cost, mechanical flexibility, chemical tunability/adjustability, and processability that allows for a simple solution-to-substrate way of PV devices manufacturing (see Part 1, 1.2). Unique physical properties of OSs are defined by the soft character of intermolecular interactions, therefore, are intrinsically unachievable in conventional IS. However, such benefits did not come without drawbacks. Among them, we can primarily note the low transport properties of OSs. The mobility of charge carriers in OSs is orders of magnitude lower than that of classical ISs^{45,101}. In addition, the process of charge separation in OSs is noticeably more difficult than in inorganic counterparts. These factors significantly limit the efficiency of OPV devices. It is therefore highly desirable to have a semiconducting material possessing efficiency of ISs and advantages associated with softness of OSs.

Metal halide perovskites (MHPs) represent a highly promising new class of materials that holds the potential to combine the best qualities of both organic and inorganic semiconductors^{102–105}.

Figure 15 shows the structural schematic of a MPH¹⁰². The MPHs are comprised of the metal halide inorganic framework (for example Pb and Br) with the atoms bonded with covalent bonds, and a mobile cation incorporated within the octahedral structure. This inner cation can be either inorganic (for example Cs⁺) or organic (for example formamidinium – FA⁺, or Methylammonium – MA⁺). Because of this metal-halide/organic cation perovskites are called hybrid materials.

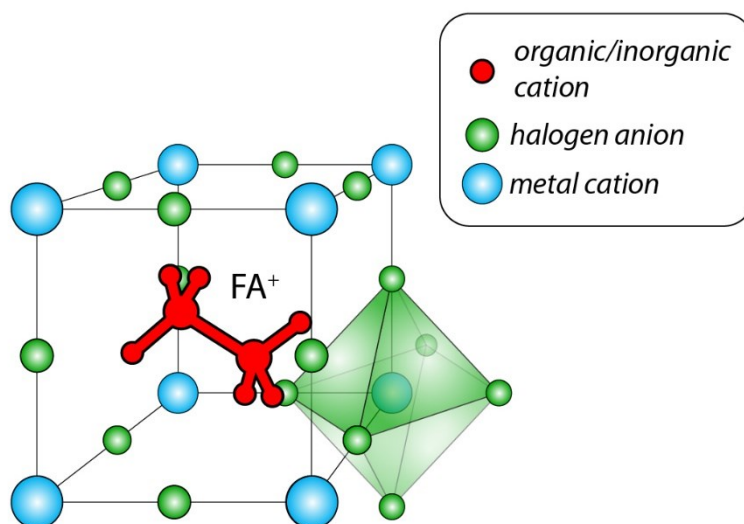


Figure 15. Metal-halide perovskite structural schematic. Formamidinium (FA⁺) cation is shown inside the inorganic octahedra as an example.

Despite the majority of atoms in MPHs being bonded with covalent/ionic bonds¹⁰⁶, this class of material demonstrates all the properties of soft semiconductors including mechanical flexibility and processability. Furthermore, it shows relatively high (compared to OSs) values of charge carrier mobilities¹⁰⁷.

Over the past decade MHPs have revolutionized the field of soft PV by demonstrating outstanding properties¹⁰⁸ and rapidly improving values of power conversion efficiency (PCE) from 3.8%¹⁶ up to 25%, which already exceeds efficiency of the best OPV devices³²! This fascinating progress was achieved by optimizing perovskite films manufacturing and passivation techniques, which are mostly aimed at an overall film quality improvement and reducing trap-mediated nonradiative losses¹⁰⁹. However, despite this inspirational progress, the fundamental physics that underlie such outstanding optical and photovoltaic properties is still intensively debated in the literature^{108,110,111}.

Recently, ion-framework vibronic interactions have been proposed to be one of the key factors affecting perovskites optical and photovoltaic properties^{108,110,112}. Supposedly, thermally activated ion fluctuations are causing large anharmonic fluctuations of an inorganic framework in response. This may result in alternation of an electronic conduction band structure and even fluctuations between direct and indirect bandgap types, which explains

extraordinary long charge carrier lifetimes observed in perovskites. Currently, these assumptions are supported by the X-ray studies¹¹², neutron scattering¹¹³ and molecular dynamic simulations^{114,115}, but comprehensive experimental confirmation is still far from being reached. In this work, Part 4 is dedicated to studying this problem with the new spectroscopic technique called VIPER (Vibrationally Promoted Electronic Resonance).

V. Rubrene single crystals

Previously, we highlighted that the efficient band-like charge transport is only observed in a handful of organic single crystals at low temperatures. In this category of high mobility organic semiconductors, rubrene (Figure 16, a) single crystal stands out in a special way. For almost two decades, it remains the highest mobility organic semiconductor with the hole mobilities reaching up to $20 \text{ cm}^2/\text{Vs}^{101}$. This impressive number exceeds the mobility of amorphous silicon ($\sim 1 \text{ cm}^2/\text{Vs}$), which is a workhorse of modern thin film electronics^{70,79}. Recently, Rubrene was also suggested as a first material for high-frequency organic electronic devices¹¹⁶.

Another advantage of rubrene is a well-developed method for obtaining ultra-pure crystals using the physical vapor transport method^{56,117} (Figure 16, b). Often, the physical properties of organic semiconductors are determined by impurity molecules that are produced as a byproduct of chemical synthesis, and which are often incredibly difficult to remove. For rubrene, the vacuum recrystallization method has been well developed, which allows it to achieve impressive SC purity (confirmed by Hall Effect and FET measurements)¹¹⁷. In addition, a method was

developed for determining crystal quality (defect concentration) with photoluminescence spectra¹¹⁸.

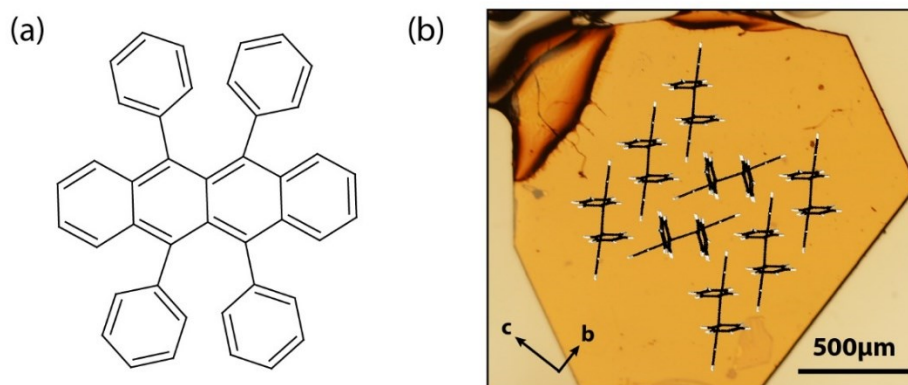


Figure 16. (a) Structural formula of the rubrene molecule. (b) Microscopy image of an orthorhombic Rubrene single crystal in correspondence with the molecular-packing schematics. There are other polymorphs of Rubrene, however the orthorhombic one has the best charge transfer characteristics.

The next advantage of Rubrene has been discovered experimentally. We found that the Rubrene SCs are possessing quite good resistance to laser-induced degradation under various conditions with several hours of exposure.

The above-mentioned factors make rubrene an excellent benchmark material for studying fundamental physical phenomena of organic crystals, such as charge transfer or exciton transport. However, Rubrene is used not only in high

conductance applications, where high mobility is the main requirement. The triplet energy level in rubrene is approximately half the singlet energy level, so it exhibits the phenomenon of singlet fission. Rubrene-based films are also used for triplet up-conversion¹¹⁹.

Part 2. Experimental techniques

This chapter provides description of the main experimental techniques that were used in the results chapters III, IV and V.

The first half of the chapter is devoted to transient absorption technique — one of the pillars of ultrafast spectroscopy. This technique is a standard tool for studying electronic dynamics in organic/inorganic semiconductors, hybrid semiconductors and beyond. In this work it was used to study the dynamics and mechanisms of singlet fission in high quality single crystals of Rubrene.

The second sub-chapter describes a new spectroscopy that has been developed recently called photoluminescence Vibrationally Promoted Electronic Resonance (photoluminescence VIPER). This spectroscopy combines the advantages of vibrational and electronic spectroscopy. By allowing selective pre-excitation with an IR pulse as a kind of marker to unravel complex electronic dynamics in complex multicomponent materials. It also has a number of other features that will be discussed in Part V.

I. Transient absorption spectroscopy

Transient absorption spectroscopy (TAS) is one of the classic techniques of ultrafast laser spectroscopy^{120–122}. It is based on a pump/probe principle in which the first pulse (pump) is photoexciting the sample, and the second pulse (probe) is probing the sample change of absorption induced by the first pulse (pump) (Figure 17).

The pump and probe pulses can be readily generated with the modern spectroscopic fs-laser systems. For example, for the most popular Titanium-sapphire (Ti:Sa) laser-based systems (800 nm central wavelength), the pump pulses may be generated with the use of optical parametric amplifiers (OPAs¹²³), or by simply doubling the photon energy with nonlinear crystals (second harmonic generation). Probe pulses are required to be broadband in spectrum to simultaneously cover the large area of absorption spectra. For this, the white-light generation scheme is typically used. The fs-pulses from the 800 nm amplifier are focused on the non-linear crystal of YAG (white light generation in near IR band: ~830-1500 nm) or sapphire (visible band) and the white light is generated within the crystal^{124,125} (if the intensity threshold is reached). Figure 18 shows the

example of the probe pulses spectra that has been used to measure TAS in Chapter 3 (in 0.3 ps to 6ns time range).

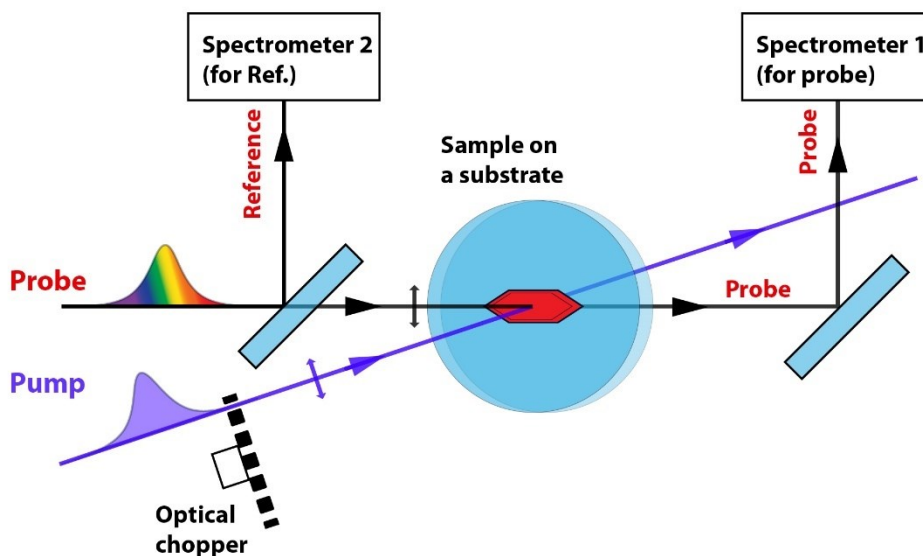


Figure 17. Schematic of a typical transient absorption spectrometer. Electronic excitation of the sample is achieved by a pump pulse (shown blue in the figure). Subsequently, changes in absorption are measured using a second wideband white light pulse - probe (shown rainbow in the figure). A second reference spectrometer is used to account for the fluctuations of the white light generation.

The experimental scheme of a typical TAS spectrometer is shown in the Figure 17. The sample is excited with the pump visible pulse, after this the photoinduced absorption of the excited species within the sample is probed with the second broadband probe pulse. The probe pulse is thereafter detected via spectrometer (1) and the received signal is corrected according to the reference spectrometer

(2). The probe pulse is normally repeated at the frequency of the laser amplifier, for example 1 kHz, and the pump pulse is repeated at half of that with the use of optical chopper. This allows capturing alternating absorption spectra of pumped and undisturbed sample, therefore capturing differential absorption spectra ($\Delta T/T$). Finally, to achieve temporal resolution, the pump pulse is shifted in time relative to the probe pulse (for example, with a delay stage), and the $\Delta T/T$ is captured for each pump/probe delay time. Thus, as a result of experiment a 2D map $\Delta T/T(t, \lambda)$ is recorded.

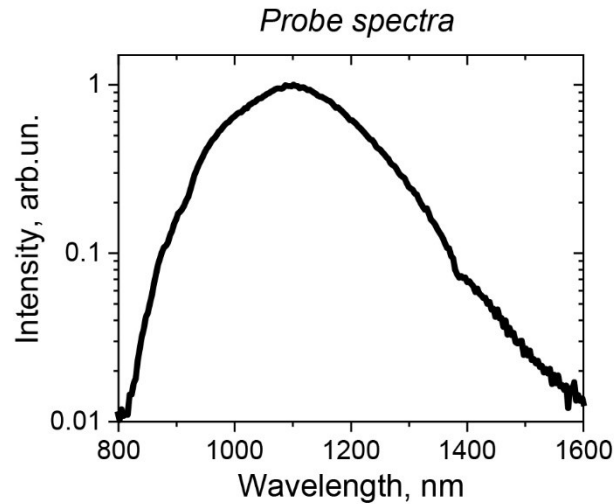


Figure 18. Example of a probe spectrum in the near-IR region.

The importance of the electric field polarizations of both the Pump and Probe pulses should also be noted¹²⁶. As follows from equations (I. 18) and (I. 19), the

probability of transition from one state to another depends on the relative orientation of the electric field and the transition dipole moment. Thus, if a sample has several electronic excitation states, then their relative TAS signal intensity will depend on the mutual orientations of the pump and probe polarization, as well as the transition dipole moment. This is especially important for highly anisotropic samples, such as organic single crystals.

II. Photoluminescence VIPER spectroscopy

One of the disadvantages of TAS is its non-specificity with respect to photoexcitation of complex materials consisting of several components. An example of such a material are, for example, OPV blends comprising of 2 or more components (donor/acceptor)³⁷. Often these components have similar optical properties and will be simultaneously excited in TAS spectroscopy, making it difficult to disentangle the signal and identify the role of specific molecules in charge/energy dynamical pathways.

In Vibrationally Promoted Electronic Resonance (VIPER) spectroscopy^{127–130}, this problem is addressed in the following manner. Initially, a desired component within the material is pre-excited with a middle infrared (MIR) pulse utilizing fingerprinting nature of the infrared activity of the vibrational modes (#1 in the Figure 19).

Secondly, the system is brought into the first electronic excited state (S1) by a visible (VIS) pulse with a suitable central wavelength (#2 in the Figure 19). The visible pulse wavelength is adjusted in a way that its energy alone is not enough to electronically excite the material. Therefore, both subsequent MIR and VIS pulses are required to make the electronic excitation within the semiconductor.

The electronic excitation is followed by PL, which is detected with an amplified photodiode in conjunction with a lock-in amplifier. In the photocurrent analog (PC VIPER), which is used with devices, after the abovementioned pulse sequence the photocurrent is measured within the device with a lock-in amplifier¹³¹.

Thus, in PL VIPER electronic dynamics is evolving along a specific scenario, programmed through IR pre-excitation. It is also worth noting that this process is very similar in nature to resonant Raman spectroscopy. Analogous to it, process 2 will be proportional to the strength of the electron-phonon interaction between the pre-excited mode and the electronically excited state¹³².

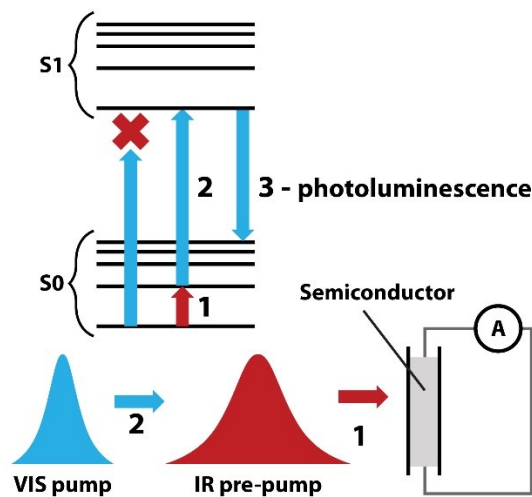


Figure 19. Schematic of the PL VIPER spectroscopy. Red arrows indicate the MIR pulse pre-excitation, blue arrows show electronic excitation via the VIS pulse.

The setup scheme for photocurrent VIPER experiments is shown in the Figure 20. The setup can be divided into 2 main parts. The first part is used to provide electronic excitation within materials with VIS pulses (Pump, blue arrows in the Figure 20), while the second part is used for vibrational pre-excitation with IR pulses (IR Pre-Excitation, red arrows in the Figure 20).

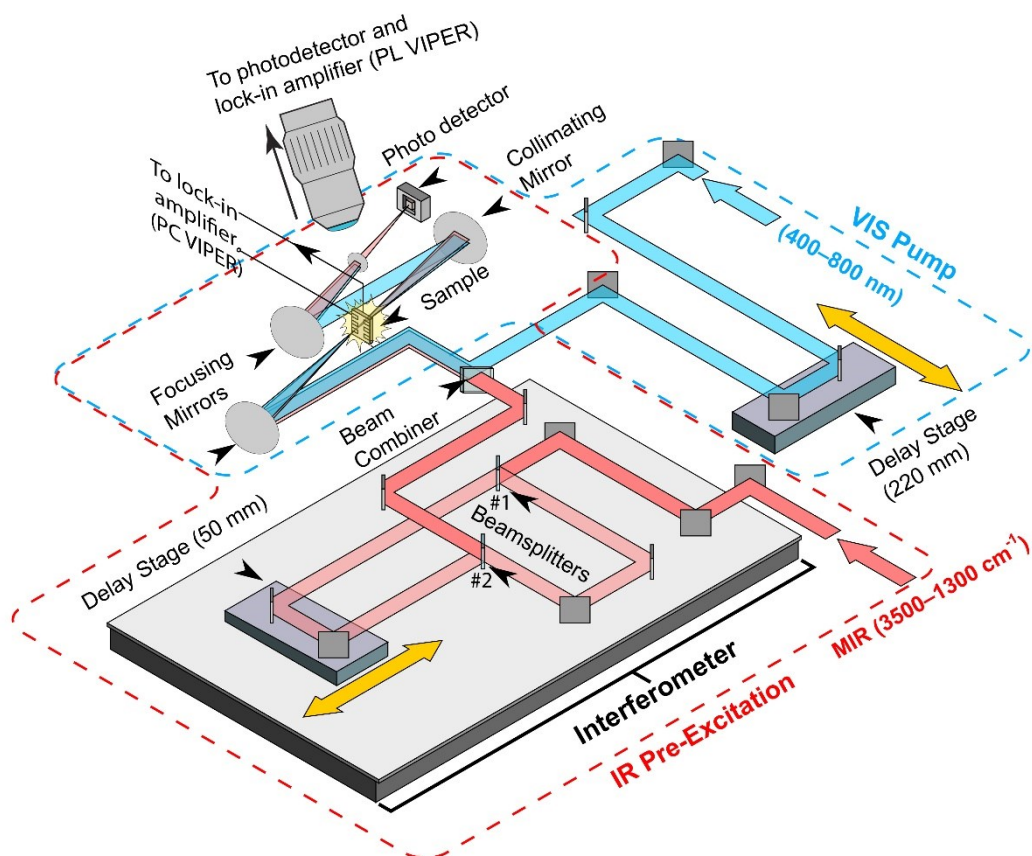


Figure 20. The photoluminescence (PL) and photocurrent (PC) VIPER setup scheme. Red line indicates the beam path of IR pre-excitation pulses, while blue line indicates the beam path of VIS pump pulses. Red and blue dashed lines delimit the

area between the visible and IR parts of the setup. The precise movement of the 50mm delay stage is provided by 635nm diode laser reference (not shown in the picture) interference.

2.1 Visible excitation

In the pump part VIS light is collimated to a delay stage that is used to control time delay between IR and optical pulses (VIS-IR delay). After this VIS radiation is collimated with the IR pulses on a beam combiner and is focused on a sample with focusing mirrors. The system is aligned by the mirrors in a manner that the IR and VIS pulses are overlapping on the sample both in space and time. Furthermore, the sample can be easily removed from the beam path to focus both IR and VIS radiation on a photo detector. This detector is used to estimate the VIS and IR pulses overlap in space and time as well as for measuring interferograms.

2.2 The MIR pre-excitation

The IR part is designed for vibrational pre-excitation of samples with IR pulses. The main component of the second part is an interferometer (Figure 20), which allows to calculate IR pulses spectrum by taking fast Fourier transform (FFT) from the measured interferograms. The use of the interferometer allows to precisely excite selected vibrational modes and selectively study the coupling of each mode with an electronic transition ($\sim 200\text{-}300\text{ cm}^{-1}$ MIR spectra full width at half

maximum (FWHM)). This is a unique feature of VIPER technique inaccessible to other conventional methods for studying these couplings (e.g. Raman Spectroscopy). First, IR light is collimated to the interferometer by mirrors. In the interferometer, IR pulses are initially split into 2 beams by a beamsplitter #1. After this, the IR pulses in the first beam are delayed in time by a 50mm delay stage relatively to the second beam. Finally, the beams are combined in the beamsplitter #2 and IR radiation is focused on a sample. Subsequently, the PL or PC is measured from the sample with a lock-in detection. As IR radiation is highly absorbed by water, the IR part of the setup (highlighted with red dashed line in the Figure 20) is purged with dry air constantly during experiments. Samples are additionally purged with nitrogen to decrease laser-induced degradation.

2.3 Data processing

In this work we used FFT to calculate VIPER spectra from collected interferograms. However, it was experimentally found that before calculating FFT of the interferograms, it is best to pre-process the interferograms in the time-domain itself to reduce the effects of the multiphoton processes in the spectrum. Further, this will be referred to as pre-processing.

Interferograms pre-processing

A typical example of the photocurrent interferogram collected from a FAPbBr₃ perovskite (1D scan: constant delay between IR and VIS pulses) is shown in the Figure 21a. The asymmetry and reduced modulation in the unprocessed data clearly show the presence of multiphoton processes during the experiment. It is natural to assume that the highest intensity of multiphoton processes is achieved, when VIS and IR pulses are strongly overlapping in time, i.e. within proximity to the interferogram maximum. To reduce the impact of multiphoton processes on the PC/PL VIPER spectrum, the interferograms are reflected at certain proximity (reflection point) to the maximum of the interference pattern (Figure 21, a). The reflection points are selected individually for each of the 2D VIPER scans depending on the final (processed) 2D maps. For example, if the multiphoton processes were too strong during the measurements, it may be necessary to move the reflection point further away from the interference maximum. As a result of this procedure (unprocessed → reflected) the multiphoton interaction region of the interference pattern is excluded from the analysis (Figure 21, a). Additionally, the noisy part of the interference pattern may be filtered out as well (multiplied by zeros, reflected → truncated, Figure 21, a).

The final step of pre-processing is the interferogram rotation (Figure 21, b): the interferogram reflection point is shifted to $t=0$ s, while the data appeared at negative time is shifted to the end of the interferogram. This step is required to avoid low-frequency modulation in the real and imaginary Fourier components after applying fast Fourier transform (FFT) to the interferogram.

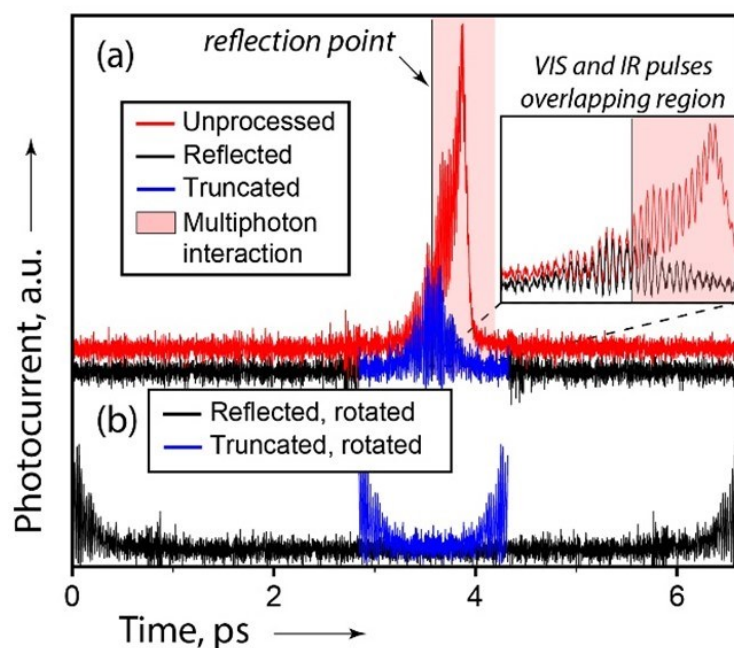


Figure 21. Pre-processing of interferograms. An example interferogram collected from a FAPbBr_3 perovskite with 5882nm (1700 cm^{-1}) IR pre-excitation and 575nm VIS electronic excitation (central wavelengths). Red line is the raw experimental data; black – the reflected interferogram with the subtracted baseline $F(t)$; blue – the truncated interferogram $F'(t)$.

Part 3. Ultrafast singlet fission dynamics in high quality Rubrene single crystals

This chapter was adapted from the pre-print titled "Interplay Between Mixed and Pure Exciton States Controls Singlet Fission in Rubrene Single Crystals" submitted for the publication in August 2023 and under review at the moment of this thesis submission. The preprint is available at [133]. Full list of authors: Dmitry R. Maslennikov, Marios Maimaris, Haoqing Ning, Xijia Zheng, Navendu Mondal, Vladimir V. Bruevich, Saied Md Pratik, Andrew J. Musser, Vitaly Podzorov, Jean-Luc Bredas, Veaceslav Coropceanu, Artem A. Bakulin. Authors contributions: DRM conducted the TAS experiments and analyzed the data; MM built the custom sub-10fs TAS setup; HN built the custom ns TAS setup; both MM and HN helped to fine-adjust the sub-10fs and ns setups; XZ and NM helped to formulate the SF model in Rubrene single crystals; VVP and VB grew the Rubrene single crystals; SMP, VC and JLB performed DFT calculations for SF rate and coherent triplet yield estimations. AAB and AJM conceptualized the study. AAB supervised the project.

Abstract

Singlet fission (SF) is a multielectron process in which one singlet exciton S converts into a pair of triplet excitons $T+T$. SF is widely studied as it may help overcome the Shockley-Queisser efficiency limit for semiconductor photovoltaic cells. To elucidate and control the SF mechanism, great attention has been given to the identification of intermediate states in SF materials, which often appear elusive due to the complexity and fast timescales of the SF process. Here, we apply 10 fs - 1 ms transient absorption techniques to high-purity rubrene single crystals to disentangle the intrinsic fission dynamics from the effects of defects and grain boundaries and to identify reliably the fission intermediates. We show that above-gap excitation directly generates a hybrid vibronically assisted mixture of singlet state and triplet-pair multiexciton $[S:TT]$, which rapidly (<100 fs) and coherently branches into pure singlet or triplet excitations. The relaxation of $[S:TT]$ to S is followed by a relatively slow and temperature-activated (48 meV activation energy) incoherent fission process. The SF competing pathways and intermediates revealed here unify the observations and models presented in previous studies of SF in rubrene and propose alternative strategies for the development of SF-enhanced photovoltaic materials.

I. Introduction

Coherent dynamics are identified to underpin ever more ultrafast processes in molecular photochemistry, from biological light harvesting^{134–136} to donor-acceptor charge transfer^{137,138} to molecular exciton multiplication processes^{84,139–141}. Frequently these processes entail conversion between optically bright and dark electronic states and the coherence is derived from strong coupling to vibrational modes. Such vibronic coupling induces mixing between bright and dark states, with these mixed states serving as key transition states or intermediates along the potential energy landscape. This framework has been widely applied to singlet fission (SF), in which a photoexcited singlet state **S** converts into a pair of triplet states **T+T**, mediated by a spin-entangled multiexciton state **TT**^{70,84,100,141–148}. The latter state exhibits key hallmarks of its mixed character—combinations of singlet-, charge-transfer-, and triplet-derived spectral signatures^{149–151}; stabilization relative to the uncoupled parent states¹⁴³; and ability to emit photons and diffuse over micron length scales despite being nominally dark and localized^{152–155}. Whether exothermic or endothermic, its formation on ultrafast timescales is found to be driven by coherent vibronic coupling^{84,141,148,156–158}.

A corollary of this mechanism is that this multiexciton character should likewise be mixed into the photoexcited **S** state, though not necessarily at the Franck-Condon point. Direct mixing of **TT** into **S** is predicted theoretically in several systems^{84,157,159,160}, but this effect has only been inferred experimentally from the observation of coherent dynamics⁸⁴. In the best-known example, the direct excitation of a coherently mixed [**S:TT**] state was initially proposed in pentacene and tetracene based on the presence of low-energy signatures in transient photoelectron spectroscopy^{139,140}. However, subsequent analysis¹⁶¹ and recent angle-resolved photoelectron spectroscopy¹⁶² indicate these systems follow the standard conversion from a pure **S** state into mixed **TT**. It thus remains unclear whether the [**S:TT**] state can be directly photoexcited, despite its established ability to emit photons^{143,149,152,153,163}.

We address this question using single crystalline rubrene of very high purity. Rubrene boasts nearly isoenergetic **S** and **TT** states and long triplet diffusion lengths^{92,164}, making it optimal for SF applications. However, the C_{2h} symmetric stacking in rubrene results in negligible electronic coupling between **S** and **TT**¹⁶⁴ (see ref. [145]), resulting in especially pronounced sensitivity to static and dynamic disorder. The dynamics of SF in rubrene have thus been controversial, with reported mechanisms ranging from <100 fs coherent to >10 ps incoherent

channels^{145,165–174}. These early studies were limited by the complex interplay between intrinsic fission dynamics related to the crystal structure and extrinsic dynamics tied to defects and grain boundaries. In addition, in the leading time-resolved studies, the assignments to **S** and **TT** states were limited by the absence of distinct spectral fingerprints not overlapped with the ground-state absorption or thermal artefacts^{145,165,175}.

Here, we study high-purity single crystals using sub-10-fs-to-ms transient absorption spectroscopy in the near-infrared, a background-free region where unique fingerprints of **S**, **TT**, and a mixed [**S:TT**] state can be readily distinguished. We recover dynamics of slow, thermally activated SF from **S** similar to prior reports^{167–172}. However, our key finding is that **S** is not the initial photo-excited state. Instead, the initial species contains unique signatures of a mixed [**S:TT**] state. Thermalization causes this state to collapse either into **TT**, which leads to a fast fission channel, or into **S**, with the latter population responsible for the slow fission channel. The branching from [**S:TT**] and its dependence on the excitation frequency reconciles the competing claims of coherent and incoherent fission in rubrene and demonstrates that even dark, multiexciton states can be directly photoexcited through strong vibronic coupling.

II. Experimental section

2.1 Single crystal growth

Rubrene single crystals were grown by multiple recrystallizations of a rubrene powder purchased from GFS Chemicals using the PVT method in a stream of ultra-high purity (UHP) He gas. Details of the crystal growth can be found elsewhere^{56,59}.

2.2 Transient Absorption

To achieve both high temporal resolution and broad time range, TA of rubrene single crystals was measured using three different setups with different time resolution and pump/probe delay range and then stitched together according to the same features in the overlapping time delay regions. The sub-10 fs resolution setup used for measurements (<10 ps) is based on the chirped mirrors compressor system described in ref. [176]. A commercially available TA spectrometer Helios (Spectra Physics, Newport Corp.) was used to measure the TA in the intermediate time delay region (>0.3 ps, <6 ns). Finally, a home-built TA spectrometer in conjunction with a q-switch nanosecond laser (Picolo, InnoLas) was used for TA measurements >1 ns. For Figure 23 in the main text, we used 400 nm (50 nJ), 430 nm (160 nJ) and 532 nm (75 nJ) pump excitation correspondingly focused on the

samples with a beam size of around 0.5 mm^2 . As a reference for the wavelength scale, we used the intermediate time delay dataset ($>0.3 \text{ ps}$, $<6 \text{ ns}$) collected with the commercial spectrometer. Wavelengths of the 2D TA maps collected with the fastest (sub-10fs, $<10\text{ps}$) and ns setups were linearly adjusted to match the mutual triplet and singlet features with the reference intermediate setup features (Helios, $>0.3 \text{ ps}$, $<6 \text{ ns}$). Relative intensity of the triplet peaks in $>1\text{ns}$ region was adjusted to match intermediate time delay dataset (Figure 23a). To balance the signal coming from the PIA of singlet and triplet excitons, probe polarization was oriented approximately 60° relatively to the OB crystal axis for the fastest ($<10 \text{ ps}$) and intermediate ($>0.2 \text{ ps}$, $<6 \text{ ns}$) setups measurements. A liquid nitrogen cryostat (OptistatDN-V, Oxford Instruments) was used for the temperature control.

III. Results and discussion

Rubrene single crystals were grown using the physical vapor transport (PVT) technique, as it is well-established to provide molecular crystals with a very low concentration of defects, thereby minimizing the influence of static disorder on charge and exciton dynamics^{56,153}. Previous work on tetracene has demonstrated that the fission rate and mechanism inferred from polycrystalline films are dominated by grain boundaries and other types of disorder and differ significantly from those in single crystals^{177,178}. To distinguish the intrinsic SF properties from extrinsic effects, it is therefore imperative to study low-defect crystalline materials. We note that the photoluminescence and other photophysical properties of organic solids, even in their highly purified single crystalline form, are very sensitive to trace impurities and structural defects^{118,119,179–181}, thus requiring special care during the material growth. Thus, for this study, we have prepared exceptionally pure PVT-grown rubrene single crystals similar to those used in the recent first demonstration of a photo-Hall effect in organic semiconductors¹¹⁷.

Figure 22a shows a photograph of a representative PVT-grown rubrene single crystal studied in this work, with the corresponding molecular packing motif

schematically overlaid on the image. The crystal is a hexagonally shaped thin plate, with its largest facet corresponding to the bc crystallographic plane (the high-mobility plane of orthorhombic rubrene⁵⁶). The hexagonal habitus was used to match the crystal axis orientation with the shape of the crystal (see Appendix C). Figure 22c shows the absorption spectra of the crystal for the incident light linearly polarized along the 0C and 0B crystallographic axes.

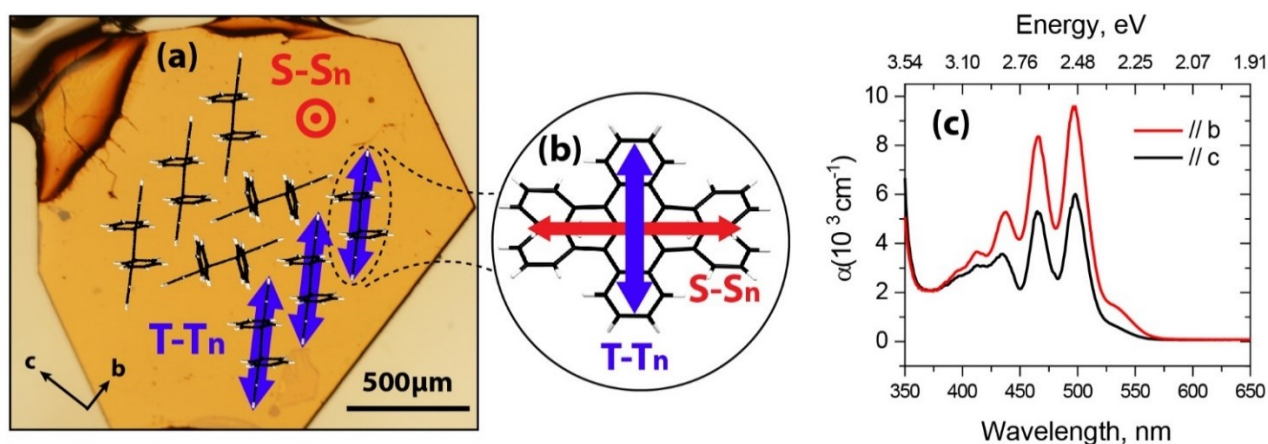


Figure 22. a) Microscopy image of the bc-plane upper facet of a rubrene single crystal in correspondence with the molecular-packing schematics. b) Illustration of a rubrene molecule with the blue [red] arrow indicating the T-Tn [S-Sn] transition dipole moment direction. c) UV-VIS absorption spectra of a rubrene single crystal for the photoexcitation polarized along b and c axes of the crystal.

We addressed exciton dynamics in the crystal using transient absorption spectroscopy (TAS) on three instruments with temporal resolutions of <10 fs, 200 fs, and 10 ns. The results were obtained using probes in the near-infrared spectral

range, which is uncontaminated by ground-state absorption and thermal artefacts^{182,183}. Moreover, this range contains unique fingerprints of the key states in the SF pathway in many other acenes: narrow vibronic resonances for **T-T_n** transitions and broad bands for **S-S_n** transitions^{156,184–186}. In crystalline rubrene, these states can be further distinguished due to the significant anisotropy that arises from the herringbone molecular packing^{56,187}, and the orthogonal transition dipole moments of the **S-S_n** and **T-T_n** transitions (Fig 1b). To balance the signal coming from the photoinduced absorption (PIA) of singlet and triplet excitons, the probe polarization was oriented approximately at 60° relative to the OB crystal axis ($\pm 5^\circ$ due to manual positioning of the crystal).

Figure 23 presents full TAS data from the single crystal shown in Figure 22a. The results from the three setups were scaled and merged to capture the full excited-state evolution from 10 fs to 50 μ s. The probe region of sub-10-fs experiments was narrower than for other experiments due to the technical limitations of supercontinuum generation. Slight shifts of shared spectral features indicate this procedure is accurate to within 5 nm. On the ns/ μ s timescale we detect a single species with 13 μ s lifetime, characterised by two sharp transitions at 878 nm and 985nm separated by a 1300 cm^{-1} spacing. These features are widely observed in solutions and thin films of polyacene derivatives^{150,151,156,184,188,189} and the lowest-

energy peak closely matches our DFT-calculated gap between relaxed **T** and **Tn** states. We thus assign these to a vibronic progression of **T-Tn** transitions of either free triplets **T** or electronically decoupled triplet pairs **T+T**. We directly observe the formation of this state within 100 fs and the slow (>ps) part of the signal growth matches the decay of a broad photoinduced absorption beyond 1000 nm. The latter band is typical of the **S** state in numerous polyacenes^{184–186,188,189} and reveals slow SF, consistent with the incoherent SF model.

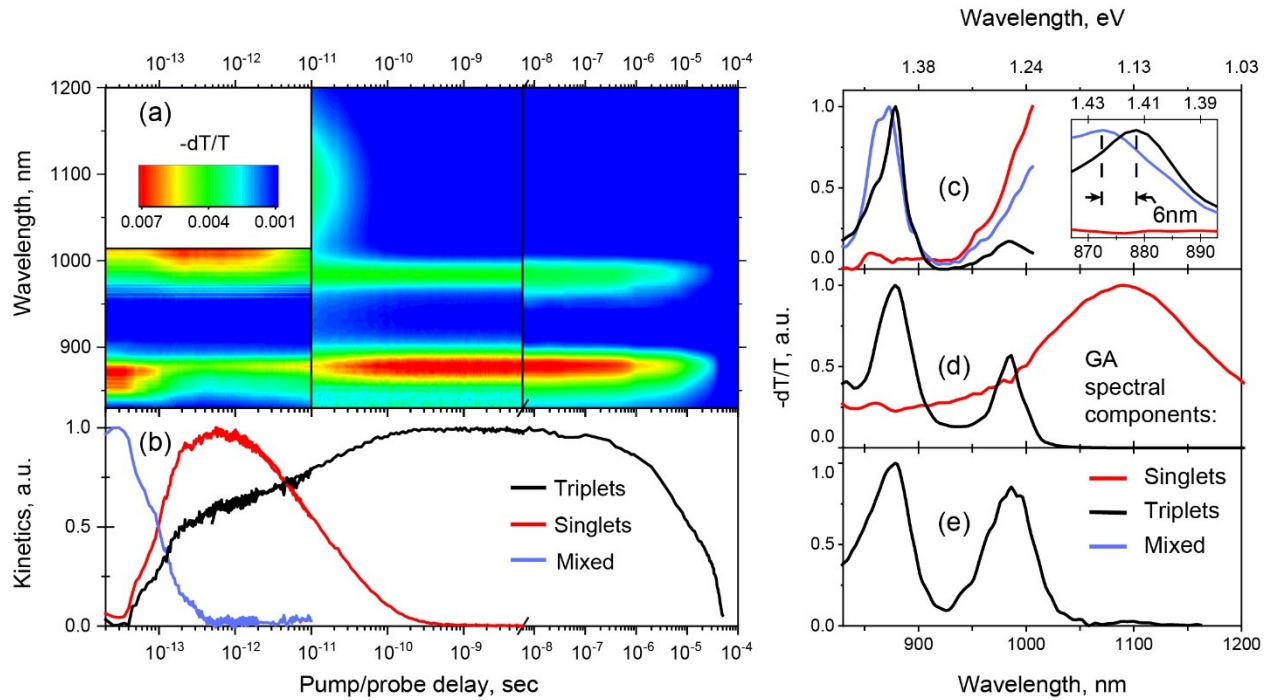


Figure 23. Room temperature transient absorption in a rubrene single crystal measured using three different setups (a) with temporal resolutions of <10 fs, 200

fs, and 10 ns. Kinetics (b) and spectra (c-e) of the S, T+T, and [S:TT] states provided by the global analysis of the experimental datasets.

However, we find that **S** is not the initial photoexcited state. On the <100-fs timescale, we resolve a distinct species with a sharp band centred at 865 nm. Closer examination reveals this feature is associated with a broad photoinduced absorption >1000 nm, and its decay tracks the rise of **S**. This qualitative analysis indicates a two-step progression: From an unknown state to **S** and from **S** to **T+T**. To identify the initial state and disentangle its interplay with the other species, we spectrally decompose the data in each temporal range using a combination of singular value decomposition and a genetic algorithm. This method permits extraction of the characteristic spectral species without any pre-determined kinetics scheme¹⁹⁰. The resulting population kinetics and spectra are presented in Figure 23b-e. We find good agreement between the extracted **T+T** spectra in all ranges and the **S** spectra corroborate the analysis above. The initial species contains a mixture of characteristics of the **T-T_n** and **S-S_n** transitions. However, it cannot be described as a simple linear combination of singlet and triplet states; for instance, the **T**-like band is shifted by 6 nm relative to **T+T**. Based on the hybrid character of this spectrum, we assign the initial species to a mixed [**S:TT**] multiexciton state. Similar hybrid states have been identified as the immediate

product state of SF in solutions and thin films^{147,149,152,156,188} and some works identify the blue-shift of **T-Tn** relative to **T+T** as a signature of the multiexciton binding energy^{143,149}. However, this is the first explicit observation that this dark mixed state can be directly photoexcited.

The population dynamics reveal two channels of triplet formation. The photoexcited [**S:TT**] state decays with ~ 80 fs time constant, resulting in parallel formation of independent **S** and **TT** components. This timescale is typical of vibrational relaxation and is consistent with the above-gap, vibrationally hot excitation in our <10 -fs experiment. Such branching should follow a coherent mechanism, with relaxation along the mixed [**S:TT**] potential energy surface into **S** or **TT** configurations weighted by their contribution to the initial wavefunction¹⁹¹. Under 400-nm excitation conditions, this coherent channel provides $\sim 40\%$ of the final triplet yield. Subsequently, the **S** population peaks at ~ 200 fs and undergoes further SF with a time constant of ~ 10 ps. This slow fission rate suggests that **S** requires energy to overcome a potential energy barrier to convert back to the mixed state [**S:TT**] or directly into **TT**. That is, the relaxed **S** is stabilized relative to **TT** and does not couple to it. To evaluate the energetics of the slow SF channel, we performed further temperature-dependent measurements in this regime.

Figure 24 shows the temperature dependence of the extracted **S** and **T** dynamics and spectra. The kinetics (Figure 24a, b) demonstrate that fission slows dramatically at low temperatures, to a time constant of 150 ps at 125 K. This result confirms the endothermic nature of the picosecond channel of SF in rubrene; though **S** and **TT** are nearly isoenergetic^{145,164,165} relaxed **S** faces a sufficient barrier to **[S:TT]** or **TT** to significantly impact the dynamics. Upon cooling, we further observe that the spectral signatures of **S** and **T** narrow at a similar pace (Figure 24c, d). At the same time, the **S** peak undergoes a blueshift, which is not observed in the **T** peaks. The energy spacing between the **T** peaks remains constant at 1300 cm^{-1} and matches the energy of the vibrational mode most coupled to electronic states, observed in Raman measurements (Figure 24e). Following previous studies, we attribute the narrow triplet signatures to significantly different degrees of delocalization for singlet and triplet excited states in organic single crystals^{192,193}.

The magnitude of the barrier between relaxed **S** and **[S:TT]** (activation energy E_a) can be estimated by applying the Arrhenius model to the fission dynamics. As shown in Figure 24f, the logarithm of the fission rate is inversely proportional to temperature over the entire measured range, indicating the thermally activated model is appropriate. Our fit yields an activation energy of 48 ± 3 meV, which is in

reasonable agreement with values previously reported for more disordered rubrene systems^{145,170,172,173,194}.

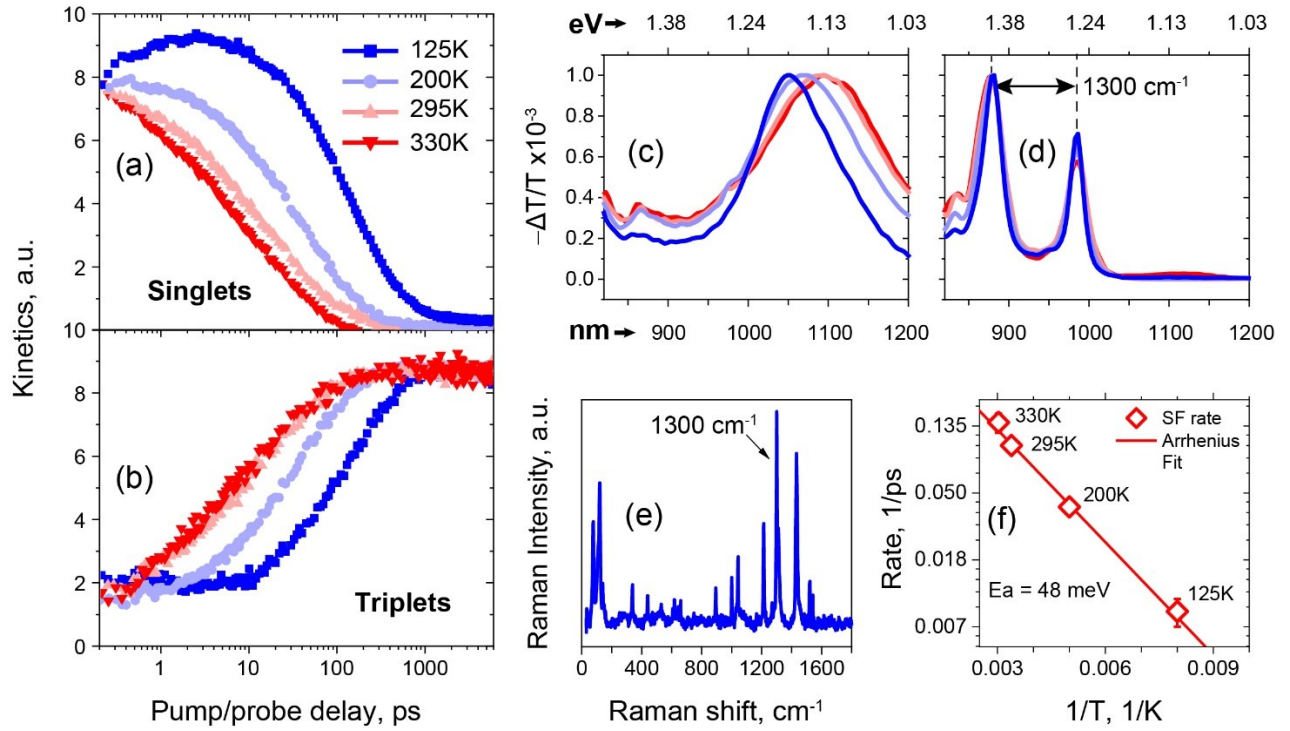


Figure 24. Kinetics and spectra of singlets (a, c) and triplets (b, d) from the global analysis of the temperature-dependent transient absorption spectroscopy of rubrene single crystals (430nm excitation). Raman spectra of a rubrene single crystal measured with the excitation polarization directed along the OB axis (e). SF rates in rubrene single crystals as a function of inverse temperature (f).

Figure 25a presents a state model of SF in defect-free single-crystalline rubrene based on our TAS findings, which reconciles the existing literature data. Excitation

with above-optical-gap photons leads to direct formation of mixed **[S:TT]** states. **[S:TT]** are partially bright states as they borrow transition dipole moment from bright **S**¹⁵². Having both **S** and **T** character, the **[S:TT]** states allow transitions into the **T_n** and **S_n** manifolds and thus possess both **S**-like and **T**-like spectral signatures in their transient absorption¹⁵¹. The **T-T_n** transition is, however, red-shifted in **[S:TT]** compared to **T** or **T+T** due to the multiexciton stabilization energy¹⁴³. In pentacene derivatives, **[S:TT]** mixing was previously shown to be promoted by the overlap of **S** and **TT** vibronic manifolds and we believe this mechanism is also present in tetracene derivatives including rubrene⁸⁴.

Within the first ~100fs after photoexcitation, the initially formed **[S:TT]** mixed states relax to either predominantly triplet-pair **TT** (and then to **T+T**), or to ‘pure’ singlet states (we estimate ~2.7 times more relaxation into **S** compared to **T**, based on the relative amounts of prompt SF). This exothermic process is the first, fast, and most likely coherent SF pathway in rubrene. Cooling to the pure **S** is followed by slow (>10ps) thermal activation of singlets over the 48 meV barrier back to **[S:TT]** and further to triplet states. Our data show that the rate of this second process is limited by thermal activation and we do not detect any further intermediates prior to **T+T**. Therefore, the conversion of **TT** to **T+T** likely occurs on a faster timescale than 10ps.

Crucially, the presented model suggests a simple way to control the branching between coherent and incoherent SF pathways. The initially excited states must be bright and therefore have substantial **S** character. However, **S** and **TT** states exist in a dense vibronic manifold and one can expect that the higher-lying states will have higher degree of mixing and higher contribution of **TT** character. This higher triplet character should increase the probability for the mixed state to branch off directly to pure **TT** via the coherent fission pathway. Indeed, we find that excitation with higher photon energy increases the relative contribution of the coherent pathway and decreases that of activated fission via **S** (Figure 25,d). While the general dynamics of the two SF pathways stay the same, importantly, the contribution to the total triplet yield from the ultrafast coherent process changes from ~17% to ~40% over our pump energy scan.

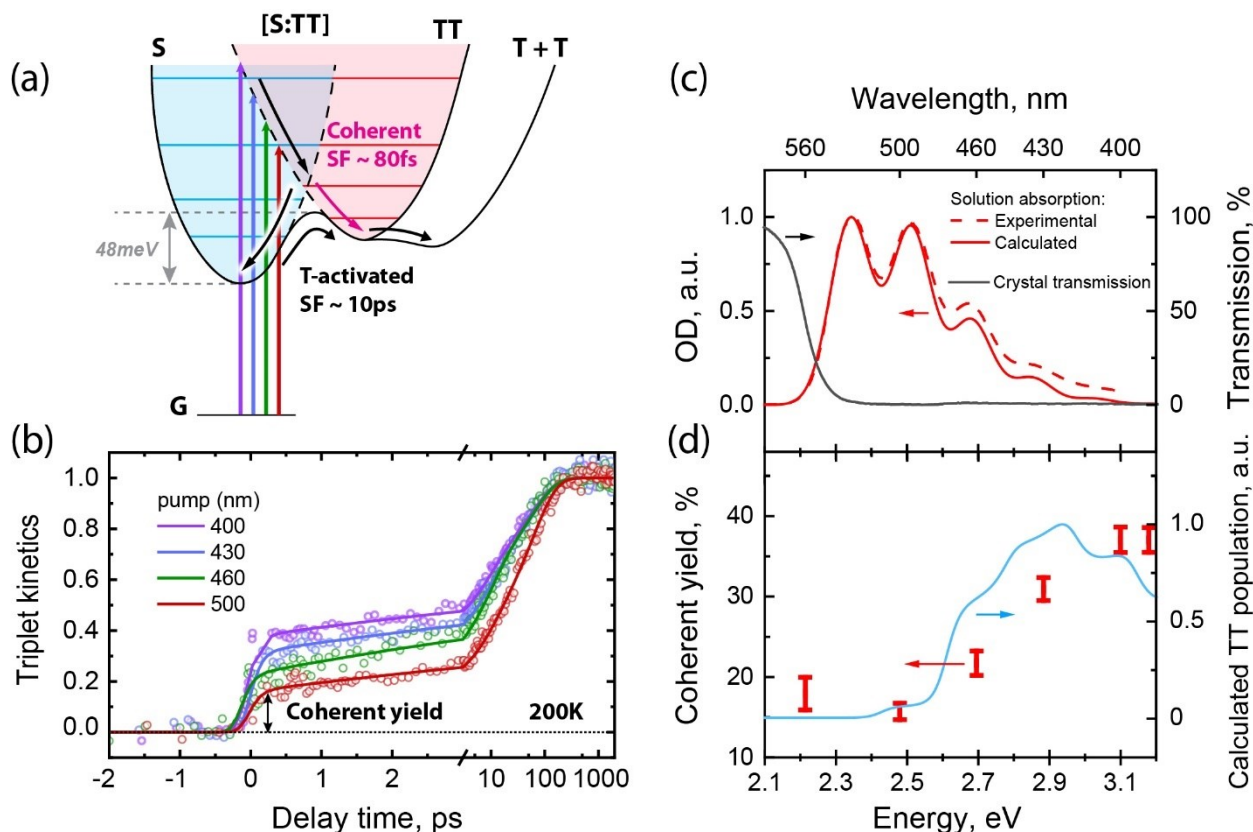


Figure 25. a) SF model for rubrene single crystals. Tuning of the excitation wavelength allows ultrafast control of the triplet states generated immediately after the excitation (coherent SF). Thick blue lines indicate photoexcitation with different pump wavelengths; curved black and pink lines point to internal interband transitions. b) Triplet SF kinetics dependence on the pump wavelength at 200K. c) Absorption spectrum of rubrene molecules in deuterated chloroform solution as calculated with the 3-state model and comparison with experiment. Experimental transmission spectrum of the crystal is shown for reference. d) Relative increase in TT state population as a function of excitation pulse energy (200K) compared with the calculated coherent triplet yield.

The analysis given above is further supported by the results of electronic-structure calculations and vibronic modelling. We first estimated the

reorganization energy related to the **S**→**TT** transition. This energy can be roughly approximated as the sum of the relaxation energies associated with the **G**→**T** and **S**→**T** electronic transitions, where **G** denotes the ground state. The calculations performed at the density functional theory (DFT) level with the global hybrid B3LYP functional and 6-31G(d,p) basis set yield a reorganization energy of about 0.3 eV (see details in Appendix C). However, our previous studies¹⁹⁵ have shown that B3LYP-based calculations usually underestimate the relaxation energies by up to 30%. In addition, we neglected the contribution to the reorganization energy due to the interactions with surrounding molecules; for non-polar systems, this contribution is typically in the range of 0.1-0.2 eV¹⁹⁶. Taking all these factors into account, the reorganization energy related to the **S**→**TT** transition is estimated to be in the range of 0.4-0.6 eV. If we were to follow the semi-classical Marcus theory, such values would lead to an activation barrier between the relaxed **S** and **TT** states on the order of 100-150 meV, i.e., two-to-three times larger than the experimental 48 meV value. However, the DFT calculations indicate that the bulk of the reorganization energy is due to non-classical (high-frequency) vibrational modes, which calls for the application of the expanded Marcus-Levich-Jortner (MLJ) model. Using this model, taking into account the DFT-derived vibrational couplings, and assuming a contribution of 0.1 eV to the classical reorganization

energy due to the surroundings, we estimate the activation energy to be 52 meV, in very good agreement with experiment. In order to reproduce the experimental rate constants, our calculations have to assume a relatively small value of 7 meV for the electronic coupling between the **S** and **TT** states.

To describe the hybridization of high-energy vibrational modes of the **S** and **TT** states, we consider a fully quantum-mechanical vibronic model¹⁹⁷ based on three electronic states (**S**, **TT**, and **G**) and two effective vibrational modes. This model treats the electronic and electron-vibrational interactions exactly¹⁹⁷, (Appendix C). Figure 25c,d presents the results of the vibronic simulations for the rubrene absorption spectrum and the contribution of the triplet **TT** state in the [**S:TT**] mixed state populated by photon absorption as a function of photon energy. Our results confirm that the direct (coherent) generation of the **TT** state in rubrene (where the reorganization energy is large) increases upon photo-exciting the vibronic and hybridised sub-levels of **S** at larger photon energies. Our calculations capture well the trend observed experimentally (Figure 25d).

We expect that a better agreement with the observed data could be achieved if additional electronic states are included into the model. We note, for instance, that the ionization potential and electron affinity energies of solid state rubrene are 5.4 eV and 2.7 eV, respectively^{198,199}. These values suggest that, when

considering the electrostatic interactions between hole and electron, the lowest charge transfer (CT) state in rubrene will appear at an energy lower than 2.7 eV. As a result, the vibrational levels of the CT state could mix with the excited vibrational manifold of the **S** and **TT** states and contribute to **TT** generation at high photo-excitation energies.

Our work potentially resolves the controversy between the two SF models for crystalline rubrene that have been debated in the literature. Coherent SF is occurring immediately after photoexcitation, as highlighted for example by Miyata et al., and the incoherent (hopping-like) SF is taking place over a potential energy barrier via thermal activation¹⁴⁵. According to the coherent SF model, an electronic wave packet formed by photoexcitation may evolve into either cold singlet or triplet-pair states via a conical intersection of the **S** and **TT** potential energy surfaces enabled by a symmetry-breaking mode; this was corroborated by the experimental observation of temperature-independent step-like PIA at 510 nm and 800 nm in the TAS kinetics, attributed to a fast (sub-100fs) formation of triplets. Our results suggest that the step-like signals may be coming from the mixed states, which possess both **S** and **T** TAS signatures. The use of high-quality samples, high temporal resolution, and wide probe range allowed differentiating **TT** and [**S:TT**] states and identifying individual states in the dynamics. We note that

another explanation of the rapidly appearing triplet signal has been proposed by Turner et al. in the framework of incoherent SF¹⁶⁵; according to that model, the rapid observation of triplet pairs with 2D electronic spectroscopy is related to weakly coupled but nearly resonant electronic energy levels of the singlet and triplet-pair states. However, this proposition, despite its attractive simplicity, is unable to explain the temperature-dependent fission rates. The scenario we put forward resolves the contradictions among the various theories by showing that both ultrafast exothermic and slow endothermic SF pathways stem from the **[S:TT]** state.

IV. Conclusion

To conclude, with multi-timescale TA spectroscopy we have tracked down the SF dynamics in high-purity rubrene single crystals, from photoexcitation (~ 10 fs) to triplet exciton decay ($\sim \mu\text{s}$). Our experiments revealed that SF in rubrene begins with the formation of a very short-lived state with a hybrid singlet/triplet character, which rapidly (~ 80 fs) coherently decays into either a singlet state or a **T+T** triplet pair. This hybrid state can be described as a vibronically-enhanced mixture of the **S** and **TT** multiexciton states. Beyond reconciling the disparate models of singlet fission in crystalline rubrene, our observation of direct excitation of a mixed [**S:TT**] state points to new ways in which SF can be optimized in endothermic systems. Here, we have demonstrated the SF pathway control via the choice of excitation photon energy. Further work may target different molecular design aspects, such as intermolecular couplings and the density of vibronic manifold, to achieve a better control of the fission mechanism and the realisation of SF-enhanced photovoltaic materials.

Part 4. Role of organic cation in formamidinium lead bromide perovskite

This chapter was adapted from the paper entitled "Ultrafast vibrational control of organohalide perovskite optoelectronic devices using vibrationally promoted electronic resonance". The full text is available at [131]. Full list of authors: Nathaniel. P. Gallop, Dmitry R. Maslennikov, Navendu Mondal, Katelyn P. Goetz, Zhenbang Dai, Aaron M. Schankler, Woongmo Sung, Satoshi Nihonyanagi, Tahei Tahara, Maryna Bodnarchuk, Maksym Kovalenko, Yana Vaynzof, Andrew M. Rappe, Artem A. Bakulin. Authors contributions: DRM conducted initial PC/PL-VIPER experiments, developed VIPER data processing software, and processed the VIPER data; NPG constructed the initial version of the PC-VIPER setup, and conducted initial PC/PL-VIPER experiments; DRM modified the setup for routine PC/PL-VIPER measurements; DRM and NM conducted wavelength-dependent control experiments; MB and MK synthesized perovskite nanocrystals; KPG, YV fabricated perovskite devices; WS, SN, and TT conducted VSFG experiments and interpreted the VSFG data; ZD, AMS and AMR performed the first-principles DFT simulations and vibrational dynamics modelling; AAB, MK, AMR, and YV supervised the project.

Abstract

Vibrational control (VC) of photochemistry through the optical stimulation of structural dynamics is a nascent concept only recently demonstrated for model molecules in solution. Extending VC to state-of-the-art materials may lead to new applications and improved performances for optoelectronic devices. Metal-halide perovskites are promising targets for VC due to their mechanical softness and rich array of vibrational motions of both their inorganic and organic sublattices. Herein, we demonstrate ultrafast VC of FAPbBr₃ perovskite solar cells via intramolecular vibrations of the formamidinium cation using spectroscopic techniques based on the Vibrationally-Promoted Electronic Resonance (VIPER). The observed short (~ 300 -fs) time window of VC highlights the fast dynamics of coupling between the cation and inorganic sub-lattice. First-principles modelling reveals that this coupling is mediated via hydrogen bonds that modulate both the lead-halide lattice and electronic states. Cation dynamics modulating this coupling may suppress nonradiative recombination in perovskites, leading to photovoltaics with reduced voltage losses.

I. Introduction

Highly selective, on-demand photocontrol of the electronic dynamics and reactivity of a material is a holy grail of photochemistry. One promising avenue to realize this control is through the selective stimulation of a material's structural and vibrational dynamics²⁰⁰. However, despite considerable effort over the last two decades, achieving vibrational control (VC) of photo reactivity has proven to be an exceptionally challenging task, requiring advances in chemistry, materials science, and ultrafast photonics. To date, only a handful of studies have demonstrated the utility of VC including the mode-selective modulation of charge transfer and carrier detrapping^{42,201–203}, triggered chemical reactions, and species-selective photochemistry^{204,205}. In these pioneering experiments however, VC has largely been limited to model chemical systems in solution; the application of VC to practically useful material systems has only been demonstrated for trapped carriers with $\sim$ ms lifetimes, diminishing the ultrafast character and selectivity of the approach⁴². Ultrafast VC measurements would provide invaluable insight into key photophysical phenomena, such as electron-phonon coupling, polaronic effects, and ultrafast structural dynamics, which in turn may lead to improvements in material properties and device performance.

One of most promising and broadly studied class of optoelectronic material today are so-called ‘hybrid organic-inorganic perovskites (HOIPs) (see Part 1, Section IV), high-performance photovoltaic materials that are inexpensive to produce, lightweight, flexible, and broadly tunable¹⁰⁴. HOIP nanomaterials also demonstrate potential in other applications, including LEDs²⁰⁶, lasers²⁰⁷, and nonvolatile memory²⁰⁸. Moreover, being a hybrid material, HOIPs combine the low electronic disorder and delocalized electronic states of inorganic semiconductors with the localized and tunable structural dynamics of organic molecules. The combination of organic and inorganic sublattices in HOIPs (Figure 26a, b) results in a rich vibrational manifold, from low-energy phonons to high-frequency intramolecular vibrations. These features, together with the rotational mobility of the organic cation^{209–212} and high structural anharmonicity^{110,213}, result in a complex dynamical behavior well-suited for VC experiments. Such experiments can, for instance, address interactions between the organic A-site cations and the surrounding inorganic cage. Despite contributing minimally to HOIPs frontier electronic states²¹⁴, organic cation dynamics may influence the optoelectronic properties of HOIPs through a variety of different means, including via modulation of the dielectric constant²¹⁵, and large polaron formation^{216,217}, among others^{218,219}. Several experimental studies have suggested that interactions

between the organic A-site cation and the inorganic cage may modulate the band-edge properties of the perovskite^{220–223}. However, the actual mechanism behind the above phenomena remain controversial, and the extent of their influence (if any) on the overall optoelectronic properties of HOIPs remains unclear^{224–227}.

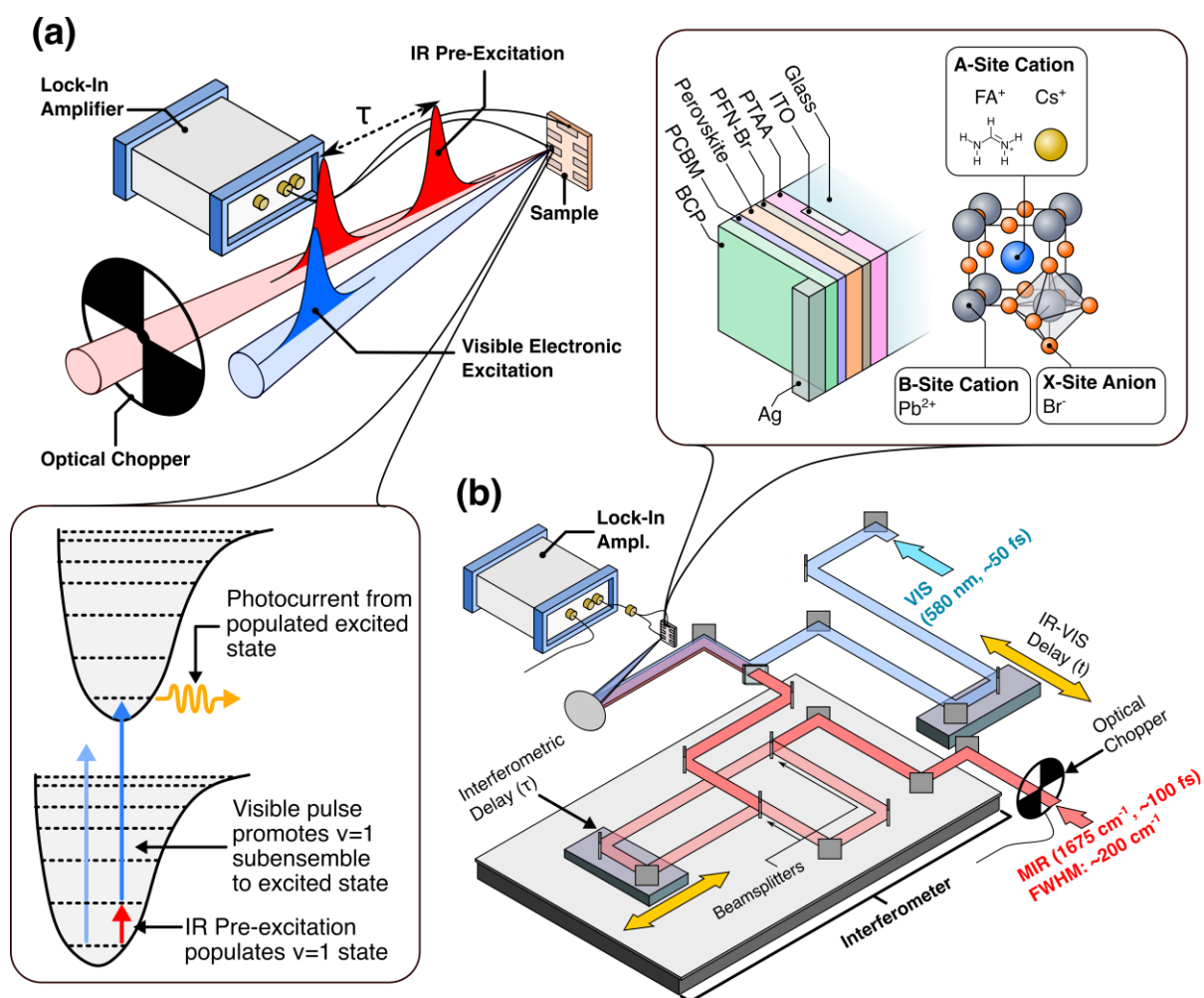


Figure 26. Overview of the PC-VIPER technique. (a) Simplified experimental setup and pulse sequence for the PC-VIPER experiment (inset: state diagram illustrating

the PC-VIPER double resonance response); (b) practical implementation of the PC-VIPER experiment, incorporating an interferometer for IR pre-excitation (inset: architecture and structure of the perovskite device employed in these experiments).

Here, we address the issue of cation-lattice interactions in HOIPs via vibrational control of perovskite photovoltaic devices. For this we realize a novel spectroscopy technique based on the Vibrationally Promoted Electronic Resonance (VIPER) approach. Conceived as an optical extension to 2D-EXSY experiments^{204,205}, the VIPER approach exhibits several advantages that make it an ideal candidate for VC, including high IR selectivity, background-free detection, sub-ps time resolution and sensitivity to electron-phonon couplings^{204,205}. To achieve direct access to the HOIPs material and device properties, we have combined VIPER with photocurrent detection (PC-VIPER) (Figure 26, a). Initially, interferometrically separated IR pulses arrive at the photovoltaic device, bringing resonant IR-active vibrational modes to their excited states. After a delay time (t), a visible pulse promotes this sub-ensemble to the electronic first excited state, which is then able to produce photocurrent. The visible pulse chosen here is off-resonant with this electronic transition such that it alone does not electronically excite the sample; only the combination of vibrational and electronic transitions populates the electronic excited state and produces photocurrent. Moreover, this process can only occur if

the target vibrational mode is coupled to the electronic transition in question and this coupling persists within the time interval between the vibrational and electronic transitions. This makes any observed signal intrinsically sensitive to electron-phonon coupling effects^{204,205}. Furthermore, changing the time-delay between the visible and IR pulses enables the monitoring of the time scales of these couplings and/or the lifetimes of the stimulated vibrational modes, while the use of an interferometer enables resolution along the IR frequency axis. By sweeping the interferometer and Fourier transforming the resulting time-domain data, any signal can be assigned to individual vibrational bands within the bandwidth of the IR pulse. The technique benefits from all the advantages of photocurrent action spectroscopies⁴¹, including operando measurements at low-power conditions, the absence of scattering and outcoupling artefacts, as well as the use of sensitive background-free lock-in detection. While PC-VIPER is the technique of choice for perovskite materials that find applications in photovoltaics, we demonstrate that luminescent perovskite nanocrystals for LED and fluorescent labeling applications can be studied by an analogous technique in which material photoluminescence is detected after the VIPER-excitation sequence (PL-VIPER). PL-VIPER is broadly analogous to the recently demonstrated

Fluorescence Encoded Infrared technique that has demonstrated high sensitivity (down to single-molecules) for model molecular systems^{228,229}.

II. Experimental section

Sample preparation procedure for devices

The systems under investigation in this study comprise bulk FAPbBr₃ and CsPbBr₃ perovskite nanocrystalline films, as well as solar cell devices. The FAPbBr₃ and CsPbBr₃ devices employed in the PC-VIPER experiments were prepared in the configuration displayed in Figure 26b, employing semitransparent Ag electrodes to enable penetration of the visible IR pulses. The fabrication of the perovskite devices was carried out in a dry, nitrogen-filled glovebox with a relative humidity of 0.5%. Initially, Glass/ITO (PsiOTech Ltd., 15 Ω sq⁻¹) substrates were sonicated at a temperature of 50 °C, first in a soap and water solution and thereafter in a mixture of deionized water, acetone, and isopropanol. Thereafter, the substrates were subjected to a 10 min oxygen-plasma treatment. A 1.5 mg/ml solution of PTAA (Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], Sigma Aldrich) in toluene was prepared and spin coated onto the surface treated glass/ITO substrates at 2000 rpm for 30 seconds; the resulting film was then annealed at 100 °C for 10 minutes. Thereafter, a 0.5 mg/ml solution of PFN-Br (Poly(9,9-bis(3'-(N,N-

dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)) dibromide, Sigma Aldrich) was spin coated onto the now annealed PTAA film at 5000 rpm for 30 seconds.

To prepare the FAPbBr₃ active layer, FABr (GreatCell Solar, Ltd.) and PbBr₂ (TCI Ltd.) were combined in a 1:1 molar ratio and dissolved in a 4:1 (v/v) DMF/DMSO (N,N-Dimethylformamide/Dimethyl Sulfoxide) mixture, resulting in a 40% wt solution of FAPbBr₃. This solution was subsequently spin-coated onto the PTAA/PFN-Br layers, initially at 1000 rpm for 12 seconds, followed by 5000 rpm for 28 seconds. In the final 3 seconds of spin coating, 200 µl of anisol was dispensed onto the film as an antisolvent. The resulting film was annealed at 140 °C for 20 minutes.

In the case of the CsPbBr₃ films, a previously reported 2-step sequential deposition method was employed¹. Both the substrates and a 1 M solution of PbBr₂ (TCI Inc.) in DMF were heated separately to 75 °C. The PbBr₂ solution was then spin coated onto the PTAA/PFN-Br film at 2500 rpm for 1 min. The resulting films were then dried for 30 minutes at 75 °C. To convert the PbBr₂ to CsPbBr₃, the film was soaked in a 15 mg/ml solution of CsBr (Sigma Aldrich) in methanol for 10 minutes at 50 °C. The films were then dried and subsequently annealed at 250°C for 10 minutes.

To apply the electron transport layers and Ag electrodes, an identical procedure was employed for both the FAPbBr₃ and CsPbBr₃ films. A 20 mg/ml solution of PCBM ([6,6]-Phenyl C61 butyric acid methyl ester, Solenne) in chlorobenzene was prepared and then passed through a 0.25 μ m PTFE filter to remove residual solid particulate. The solution was then dynamically cast onto the active layers at 2000 rpm for 30 seconds. The film was then annealed at 100°C for 10 minutes. A bathocuprene (BCP, Sigma Aldrich) hole blocking layer was then spin coated onto the PCBM film from a 0.5 mg/ml BCP/isopropanol solution at a speed of 4000 rpm for 30 seconds. After drying, silver electrodes were evaporated onto the film at a rate of 0.1 Angstrom/s to a thickness of 18 angstroms.

Sample preparation procedure for films

To produce the oleylammonium bromide (OLAmBr) precursor, 12.5 mL oleylammonium (OLAm) was mixed with 100 ml EtOh in a flask and cooled in an ice/water bath. Thereafter, 8.56 mL HBr (48% aqueous solution) was added. The reaction mixture was left to react overnight under nitrogen flow. The resulting solution was dried in a rotary evaporator and the remaining precipitate was washed multiple times with diethyl ether. The resultant white OLAmBr powder

was dried under vacuum at room temperature for several hours and then stored in a glovebox.

To synthesis the FAPbBr₃ nanocrystals, 76 mg lead (II) acetate trihydrate (0.2 mmol) and 78 mg formamidinium acetate (0.75 mmol) were dispersed in a mixture of 8 mL ODE and 2 mL OAc, heated to 50 °C , and then dried under vacuum for 30 min. Thereafter, the reaction mixture was heated to 130 °C and a separately prepared solution of 266 mg OLAmBr (0.8 mmol) in 2 mL anhydrous toluene was injected into the reaction flask. To prepare the OLAmBr/toluene solution, the mixture was heated to 40-50 °C and held at this temperature for approximately 30 s, after which the reaction mixture was cooled in an ice/water bath.

To obtain purified NCs from the resulting crude solution, 16 mL of methyl acetate was added, and the mixture was centrifuged at 12.1 krpm for 5 min. The resulting supernatant was discarded and the remaining precipitate redissolved in toluene (5 mL). This solution was centrifuged a second time at 3 krpm for 2 min. In this case, the supernatant was retained for the DDAB treatment, with any precipitated NCs discarded.

To DDAB treat the purified FAPbBr₃ nanocrystals, 5 mL toluene was added to FAPbBr₃ colloidal solution prepared described above. Thereafter, 0.1 mL of OAc

and 0.54 mL of DDAB (0.05 M in toluene) were added to 10 mL colloidal solution of FAPbBr₃ NCs; the resulting mixture was stirred for 1 h., followed by precipitation with 16 mL ethyl acetate. The resulting suspension was centrifuged at 12.1 krpm for 3 min. The precipitate was redispersed in 2.5 mL toluene and this solution was additionally filtered through a 0.45 μ m PTFE filter.

To deposit the FAPbBr₃ nanocrystals, CaF₂ substrates (12 mm diameter, 1 mm thickness, EKSMA Optics) were treated with O₂ plasma to improve wetting. The concentrated NC inks were drop-casted from solution onto the cleaned substrates in a N₂ atmosphere. The thickness of the thin films were determined to be ~300 nm by UV-vis ellipsometry.

Photocurrent and photoluminescent VIPER experiments

The Incident Photon to Converted Electron (IPCE) spectra of the FAPbBr₃ device Figure 27, a) exhibits a sharp band edge at 550 nm with efficiencies of 60—80% above the band edge. To ensure minimal direct absorbance of the visible pump pulse absent IR pre-excitation, the center wavelength of the pump was set at approximately 580 nm, well below the onset of efficient photocurrent generation.

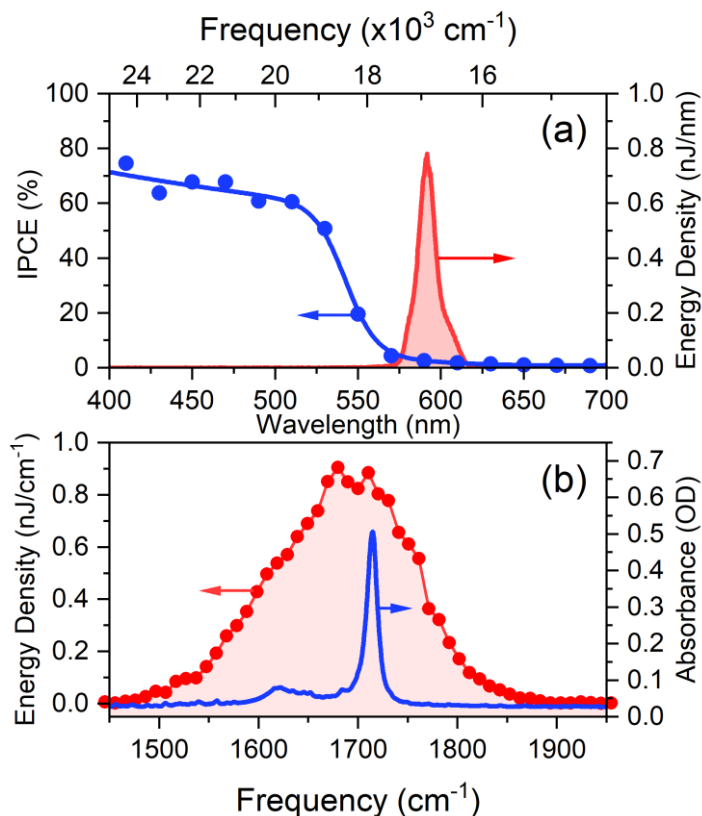


Figure 27. Characteristics of FAPbBr₃ and choice of optical pulses. (a) IPCE spectrum of an FAPbBr₃ device (blue), along with the spectrum of the visible electronic excitation pulse (red shaded) employed in this work; (b) IR absorption spectrum of FAPbBr₃ (blue), overlaid on the spectrum of the IR pre-excitation pulse (red) employed in this experiment.

The IR spectrum of an FAPbBr₃ film (Figure 27, b) shows a weak band at $\approx 1615 \text{ cm}^{-1}$ and a strong line at $\approx 1715 \text{ cm}^{-1}$, corresponding to N-H scissoring ($\delta_1(\text{NH}_2)$) and asymmetric stretching of the N-C=N double bond ($\nu(\text{N-C=N})$) of formamidinium (FA), respectively²³⁰. IR-ATR spectra of the full FAPbBr₃ and CsPbBr₃ devices show no other vibrational modes over this measurement range. To avoid the IR

absorption and dispersion in the glass, indium tin oxide (ITO), and Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) charge extraction layer, we illuminate the perovskite through semitransparent top Ag electrodes during PC VIPER experiments. In both PL and PC VIPER experiments, the VIS and MIR powers were 50uW (12.5nJ) and 300uW (75nJ per each IR pulse) correspondingly at the sample position. Focus spot at the sample position was ~0.5mm, in all experiments the samples were purged with nitrogen gas flow.

Linewidth analysis of the $\nu(\text{N-C=N})$ mode

We have performed the analysis of vibrational lineshape to estimate the typical timescale of polarisation decay after interaction of the sample with IR pulse. We can obtain the relaxation of the vibrational mode via the Fourier Transform of our IR lineshape. Figure 28a displays the $\nu(\text{N-C=N})$ mode at ca. 1720 cm^{-1} acquired in both transmission and ATR mode—in both cases we observed relatively minor changes in the vibrational lineshape, although the overall widths of the two lines are similar. Fourier transformation of these vibrational lines yields the relaxation dynamics given in Figure 28b, in both cases, the relaxation of the vibrational line is approximately 850—870 fs depending on the measurement method (transmission vs ATR).

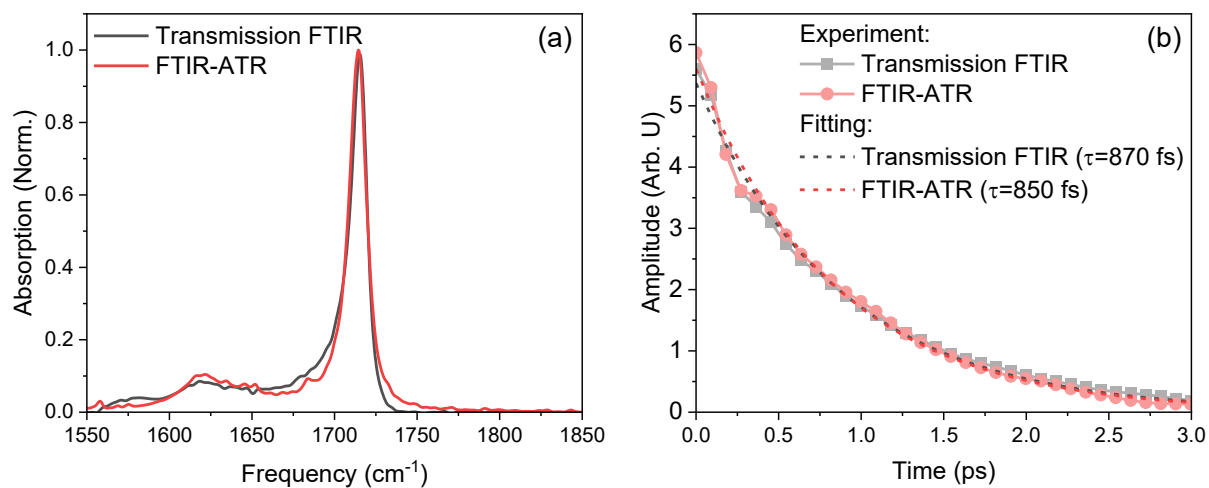


Figure 28. Linewidth analysis of the 1720 cm^{-1} vibrational mode of FAPbBr₃. (a) Lineshapes of the 1720 cm^{-1} feature acquired in transmission and ATR mode; (b) calculated vibrational relaxation dynamics obtained through fourier transform of the features in (a).

III. Results and Discussion

3.1 PC and PL VIPER experiments

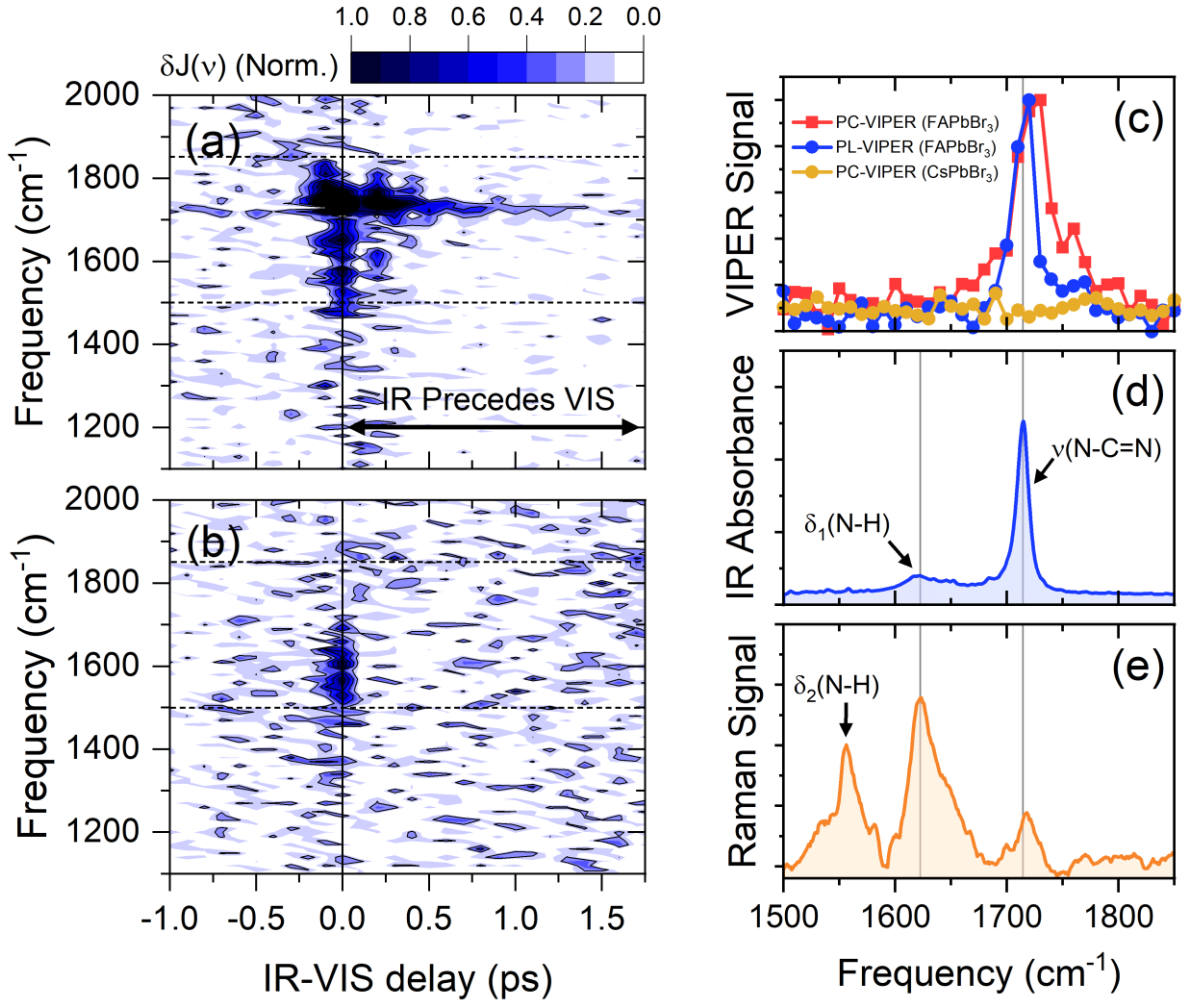


Figure 29. PC-VIPER results for FAPbBr₃ and CsPbBr₃. (a, b) PC-VIPER maps for (a) FAPbBr₃, and (b) CsPbBr₃. The black arrow in (a) denotes where the IR pulse precedes the visible pulse, whilst the horizontal dashed lines denote the approximate spectral width (>10% peak amplitude) of the IR pulse. (c–e)

assignment of PC-VIPER data to known vibrational modes: (c) one-dimensional PC-VIPER spectra for FAPbBr₃ and CsPbBr₃; (d) IR spectrum of FAPbBr₃; (e) Raman spectra of FAPbBr₃. The frequencies of the $\delta_1(\text{NH}_2)$ and $\nu(\text{N-C=N})$ modes (approximately 1620 and 1715 cm^{-1} , respectively) are demarcated in grey. A 1D PL-VIPER spectrum (see Figure 28, a) is also displayed in (c); in all cases, the 1D traces are obtained by averaging the 2D maps in Figs. 3(a) 3(b), and 4(a) between 100 and 1000 fs.

Figure 29 displays two-dimensional PC-VIPER maps for the FAPbBr₃ and CsPbBr₃ photovoltaic devices. The maps are obtained by scanning the interferometer delay (τ) for a range of IR-VIS delays (t). Thereafter, the time domain signal is Fourier-transformed along the τ axis to produce an IR action spectrum^{42,231}.

Within the pulse overlap regime (± 50 fs), both materials exhibit a broad featureless signal centred at $\approx 1600 \text{ cm}^{-1}$, attributable to residual non-resonant two-photon effects. This broad signal was greatly suppressed via the time-domain phasing and filtering process¹³¹ but could not be fully eliminated. Beyond the pulse-overlap time region (i.e., > 80 fs, where the infrared vibrational pre-excitation arrives before the visible electronic pump), the nonresonant signal for FAPbBr₃ (but crucially not CsPbBr₃) gives way to a single sharp line, centred at approximately $1720 (\pm 10) \text{ cm}^{-1}$. The agreement of this line with the frequency of the $\nu(\text{N-C=N})$ vibration²¹² of FA (Figure 27, b), alongside the absence of a similar line for CsPbBr₃, suggests that this feature originates from the FA vibration. We

assign this feature to vibronic coupling between the FA-cation's $\nu(\text{N}=\text{C}=\text{N})$ vibrational mode and the electronic state of perovskite. Interestingly, despite the IR pre-excitation spectrum covering both features (the $\nu(\text{N}=\text{C}=\text{N})$ and the $\delta_1(\text{NH}_2)$ modes) only the line at 1720 cm^{-1} is observed. Intuitively, any VIPER-active modes should be both IR and Raman active, as IR activity enables population of the vibrationally excited state, and (resonance) Raman activity is associated with the strength of vibronic coupling¹³². However, considering that we use non-resonance Raman for analysis, and given the complexity of the interaction mechanism, more complex selection rules may be in place.

To confirm that the observed vibronic phenomenon exists across different perovskite materials, we repeated VC experiments on FAPbBr₃ nanocrystals. Such nanocrystals are known to have outstanding photoluminescent properties, and we therefore employed in PL-VIPER experiments (for details, see Part 2, Section II). The experimental parameters (e.g. pulse spectra, excitation fluences) and data analysis approach were identical to the PC-VIPER experiments described above.

As with PC-VIPER, a single sharp vibrational line at 1720 cm^{-1} , corresponding to the $\nu(\text{N}=\text{C}=\text{N})$ mode of FA, is observed in the PL-VIPER experiments (Figure 30) with a distinct absence of the $\delta_1(\text{NH}_2)$ mode also covered by the pulse. PC- and PL-VIPER responses exhibit similar line shapes (Figure 29, c), similar dynamics (Figure 30, b).

The slight discrepancy in decay times (240 ± 30 fs from PL-VIPER vs. 280 ± 20 fs for PC-VIPER) may be due to the differing material morphologies and minor ligand effects in our FAPbBr₃ nanocrystals compared to bulk FAPbBr₃. Nevertheless, these findings indicate that we have been able to monitor the same VC effect using both photocurrent (PC) and photoluminescence (PL).

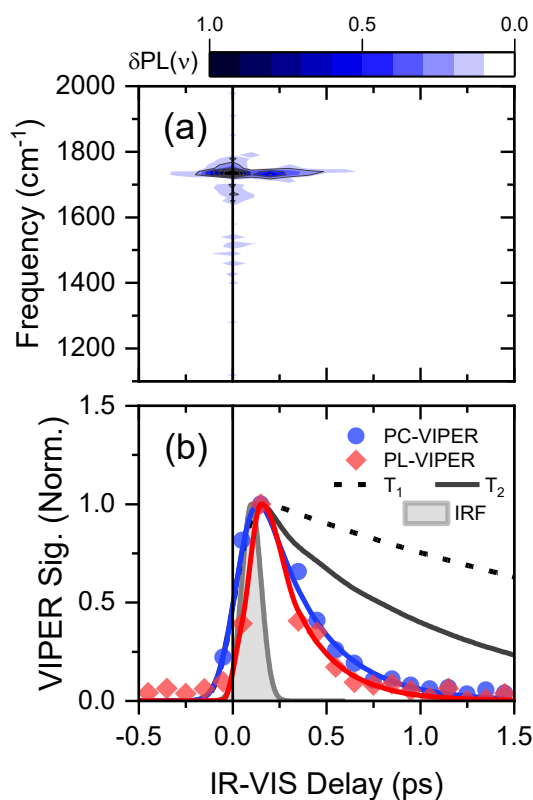


Figure 30. Results of PL-VIPER in FAPbBr₃ and VIPER dynamics: (a) PL-VIPER map for FAPbBr₃; (b) Kinetics of the PL-VIPER and PC-VIPER signals at 1720 cm⁻¹. The population relaxation (T_1) and free induction decay (T_2 , estimated from linewidth analysis, see above) are shown for comparison. The instrument response function

(IRF) in (b) was estimated from a Gaussian fit of the non-resonant response of CsPbBr₃.

We now address alternative explanations for the emergence of this signal. We compared the IR spectra of the full FAPbBr₃ and CsPbBr₃ devices (see Appendix D) to those of the FAPbBr₃ films given in Figure 27 and found no substantial difference indicating the signal purely originates from the perovskite active layer. We can rule out an anti-Stokes Raman-like effect, in which the off-resonant visible photons are inelastically scattered from excited vibrational state because the lifetime of our signals is substantially shorter than the lifetime of the vibrational mode previously observed via 2DIR spectroscopy²¹² or estimated from lineshape analysis (Figure 30, b). By a similar token, the persistence of the VIPER signal is also too short to emerge from vibrational sum-frequency generation (VSFG), whose temporal profile follows the free induction decay of the vibration^{232–234}. We estimate the vibrational dephasing of the 1720 cm⁻¹ mode to be ~850—870 fs, based on the linewidth analysis of the IR absorption spectrum, which is significantly longer than the 280-fs lifetime of our PC- and PL-VIPER signals (Figure 30). Moreover, the independently measured VSFG spectra of our FAPbBr₃ films exhibit a negligible signal at 1720 cm⁻¹¹³¹. Collectively, these results suggest that the VIPER signal decay is controlled by some other process, rather than simply the

population or dephasing of the vibrational state. Finally, sample heating²²⁷ effects on the band edge can be discarded due to the rapidity with which the observed signals grow in (<100 fs) and dissipate (sub-ps, cf. >1 ns for sample heating effects). Consequently, we conclude that vibronic coupling between the cation and the electronic state of the perovskite provides the most plausible explanation for the observed VC phenomenon.

3.2 The Origin of Vibronic Coupling

The observed VIPER kinetics reveal the nature of the vibronic coupling phenomenon behind the PC- and PL-VIPER signals. The rapidly decaying PC- and PL-VIPER signals (Figure 30) are ~ 10 times faster than the population relaxation rate for the same mode previously observed for FAPbI₃ (2.8 ps)²¹², and roughly 3 times faster than the vibrational free induction decay¹³¹, suggesting that its dynamics depend on other processes within the material and match much better the timescales of the rotational dynamics of the FA cation. Cation rotation, given the highly directional nature of FA-Br hydrogen bonds²³⁵, can significantly influence the interaction between the FA ions and the inorganic lattice, which determines the frontier electronic states of the perovskite. Intriguingly, the ≈ 280 fs lifetimes of VIPER signals are comparable to the 300–400 fs 'wobbling times' of

rotational motions observed for MA and FA perovskites²¹². This indicates that the re-orientation of the organic cation may dictate the timescales over which the vibrational states of the cation and electronic states of the perovskite lattice is coupled. This is supported by previous studies highlighting the importance of hydrogen bonding on the structural dynamics of the PbBr₃ sublattice¹¹², as well as a recent 2DIR report that finds agreement between the rate of spectral diffusion of MA-containing perovskites and the faster ‘wobbling’ timescales of the cations²³⁶.

Identifying the mechanism of the vibronic coupling evolution should consider the electronic structure of the perovskite, the rotational dynamics of the FA cations, the interaction between the cations and the inorganic sublattice, and the vibrational dynamics of FA. We anticipate that the kinetics of our VIPER signal should depend on the dynamics of electron-phonon coupling that can be modulated by all the above processes. To gain atomistic insight into the origin of the vibronic coupling phenomena observed in our PC- and PL-VIPER experiments we performed a series of ab initio molecular dynamics (MD) simulations on a 2x2x2 perovskite supercell¹³¹.

We first used MD to quantify the hydrogen bond dynamics and correlate them with the dynamics of vibronic coupling observed in VIPER experiments. At each

time step of the simulation, we calculated the distances between the four hydrogen atoms on the -NH₂ groups of FA and their nearest neighboring Br⁻ ion. The dynamics of the H•••Br bond distance predominantly consist of fluctuations about a local equilibrium value, with occasional drops in the H-Br distance that are almost immediately followed by a return to the equilibrium¹³¹. Previous ab initio studies have ascribed this behaviour to a stochastic formation and breakage of hydrogen bonds between the FA and the surrounding PbBr₃ cage¹¹². Statistical analysis of these events yields the ensemble-averaged dynamics of hydrogen-bond breakage, expressed as the evolution of the N-H•••Br separation following hydrogen bond formation¹³¹. A rapid initial increase in the bond distance shortly after hydrogen bond formation accounts for much of the H•••Br bond evolution. The dominant time scale of this evolution is ≈300 fs, in good agreement with the wobbling times of other FA perovskites, demonstrating a correlation between the hydrogen bond dynamics and the rotational dynamics of the organic cation.

The complete rationalization for our experimental results is presented in Figure 31. Figure 31(a–c) match the kinetics of experimentally obtained VIPER signal to three of the dynamic properties of the organic cation. Specifically, we compare the experimental VIPER kinetics (black dashed line) to the orientational anisotropy decay of the FA vibration in FAPbI₃ perovskite²⁰⁹ (Figure 31, a), the simulated

dynamics of hydrogen bond breakage from ab initio MD (Figure 31, b), as well as the time-resolved cross correlation between the Pb-Br and N-H...X bond distance obtained by Singh et al (Figure 31, c)¹¹². The PC-VIPER data broadly matches both the experimental rotational dynamics observed via 2DIR anisotropy decays and the MD results. In particular, the strongly negative cross-correlation (Figure 31, c) implies that a shortening of the N-H...X bond distance is coordinated with an elongation of the Pb-Br bond distance. This suggests that hydrogen bonds between the organic cation and the inorganic lattice induce a distortion of the latter. Thus, a picture emerges in which N-C=N vibration of the cation affects N-H...X hydrogen bonding, which in turn may alter the electronic states of the perovskite through distortion of the inorganic cage. The effect of the N-C=N vibration on hydrogen bonding may not be that surprising since the vibrational motion of the nitrogen atoms affects the hydrogen atoms involved with H-bonding. Additionally, the relative softness and anharmonicity of HOIPs, combined with the rotationally mobile and anisotropic nature of the organic cation, opens up the possibility of dynamic fluctuations in the inorganic cage driven by the organic sublattice. The reverse process—in which inorganic lattice oscillations drive cation reorientation—has been invoked to explain differences in the rotational dynamics of the organic cation in a variety of HOIPs^{209,237}. Some studies

also suggest that hydrogen bonds between the organic cation and halide anions distort the PbX_3 octahedra indirectly influencing the material's optoelectronic behavior¹¹². We note however, that our computational approach cannot account for the vibrational relaxation of the $\nu(\text{N}=\text{C}=\text{N})$ mode, which is a significant loss pathway for VIPER signals.

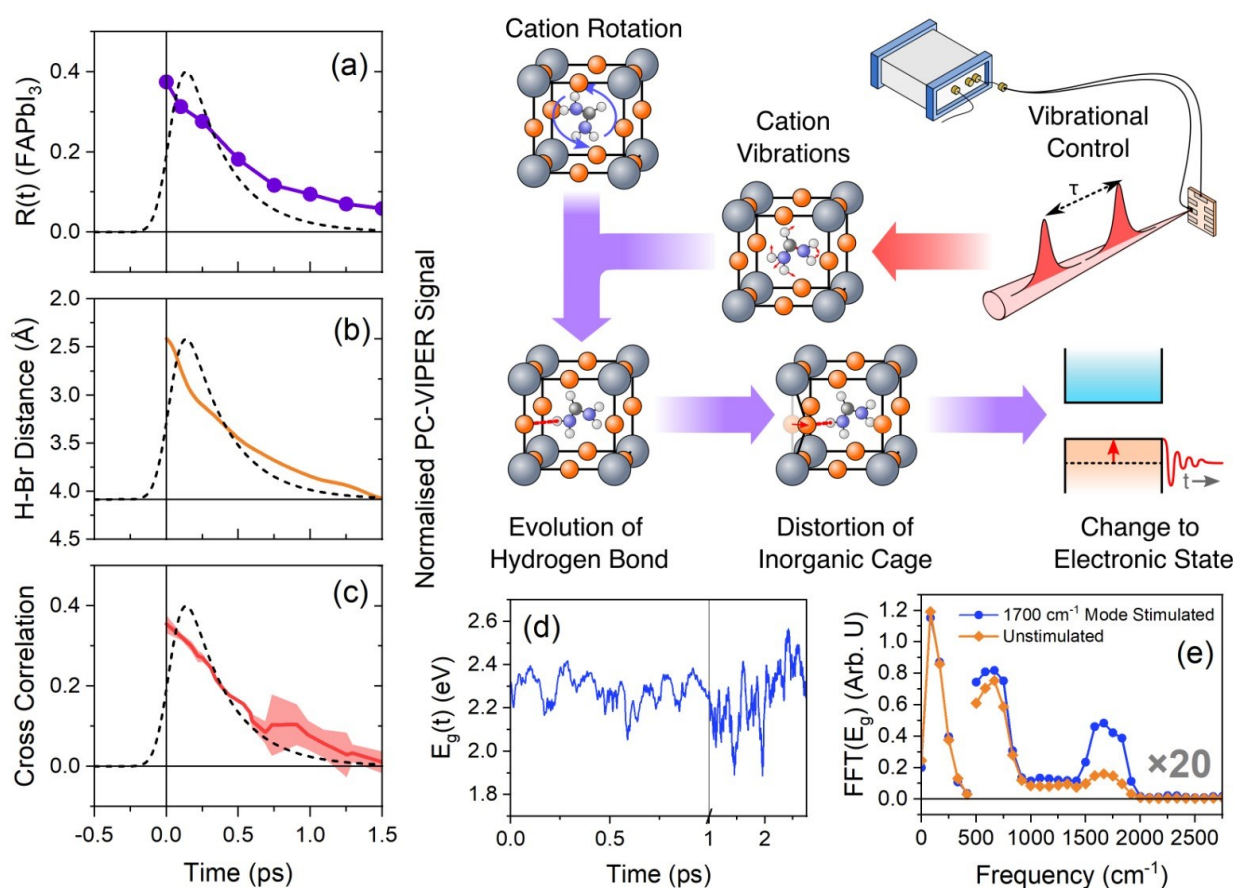


Figure 31. Rationalization of the VIPER effect in FAPbBr_3 : (a–c) comparison of PC-VIPER kinetics (dashed lines) to (a) the previously experimentally determined rotational anisotropy of the FA ion in FAPbI_3 ; (b) the *ab initio* picosecond dynamics

of the H-Br bond distance; (c) the time-resolved Pb-Br/H-Br cross correlation function obtained from *ab initio* molecular dynamics simulations performed by Singh et al. in ref. [112]. (d, e) analysis of the band gap dynamics obtained from the *ab initio* molecular dynamics simulations described in this work: (d) Blue: Band gap of FAPbBr₃ for a representative trajectory following perturbation of the $\nu(\text{N}=\text{C}=\text{N})$ mode; (e) power spectrum of the oscillatory component of the band gap fluctuations displayed in (d) the blue curve represents the average of the power spectra of the five trajectories in which the $\nu(\text{N}=\text{C}=\text{N})$ mode is stimulated; the corresponding averaged power spectrum for the five unperturbed trajectories is given in orange.

The *ab initio* modelling at equilibrium is unable to measure the direct effect of the $\nu(\text{N}=\text{C}=\text{N})$ dynamics of the organic cation on the electronic properties of the perovskite, as the amplitudes of the relevant mid-IR ($\approx 1700 \text{ cm}^{-1}$) vibrational states is negligible at the simulated temperatures. We therefore modified the above approach by adjusting atomic velocities along the normal modes corresponding to the $\nu(\text{N}=\text{C}=\text{N})$ vibration of the FA ion, which we identify *via* phonon calculations. The adjustment amounts to three quanta of the $\nu(\text{N}=\text{C}=\text{N})$ vibrational mode per supercell to simulate the IR pulse excitation in the PC-VIPER and PL-VIPER experiments¹³¹. In total, we ran ten individual trajectories—five in which the $\nu(\text{N}=\text{C}=\text{N})$ mode was stimulated, and five in which no stimulation was introduced. The representative evolution of the perovskite band gap for one such trajectory following stimulation of the $\nu(\text{N}=\text{C}=\text{N})$ modes is given in Figure 31d, and shows both slow, large amplitude fluctuations and variation on faster timescales.

Fourier analysis of the band gap dynamics reveal the involvement of multiple modes at *c.a.* 100, 700, and $\approx 1700\text{ cm}^{-1}$ (Figure 31, e). We assign the modes in the $<280\text{ cm}^{-1}$ low-energy band to motions of the PbBr_3 octahedral cage, while the modes in the $300\text{--}1000\text{ cm}^{-1}$ region are commonly ascribed to hybrid modes of the organic cation rotations coupled to motions of the inorganic lattice²³⁷. The dominant mode is the oscillation at $\approx 100\text{ cm}^{-1}$, suggesting that modulation of the band gap is primarily driven by fluctuations of the inorganic cage. The mode at $\approx 1700\text{ cm}^{-1}$ is likely the intramolecular $\nu(\text{N-C=N})$ modes of FA, which matches well the one we experimentally access by IR excitation in VIPER experiments. Comparing the Fourier amplitude of this $\approx 1700\text{ cm}^{-1}$ mode for trajectories with and without stimulation we observe that the relative contribution of $\nu(\text{N-C=N})$ mode is strongly and selectively enhanced, highlighting its coupling to the bandgap of the perovskite. We note however that there are other significant differences between the orientational selectivity of our VIPER experiments *versus* our AIMD simulations arising from the polarization of our pulses that also needs to be considered¹³¹.

Our results carry significant implications for perovskite-based optoelectronic devices. Previous studies have emphasized the impact of the A-site cation on the electronic structure of HOIPs inhibiting the cooldown of hot carriers²³⁸ and our

findings elucidate the mechanistic picture behind this phenomenon. Moreover, we note that, if high-frequency phonons can be used to stimulate sub-bandgap absorption, then the opposite pathway (electronic relaxation through intramolecular modes of the organic cation) may also be possible. This could suggest that the coupling of the high-frequency vibration of the cation to the electronic states in HOIPs introduces facile nonradiative pathways for carrier relaxation and so impacts the intrinsic nonradiative relaxation of photogenerated carriers. In HOIP solar cells, nonradiative losses have traditionally been the result of trap-mediated recombination, as well as losses at interfaces within the device stack and/or at the surface²³⁹. However, with the development of new strategies for the passivation of defects, losses due to these extrinsic factors have reduced^{240,241} making the role of intrinsic nonradiative recombination dominant. Our findings suggest a natural route for controlling the coupling between the organic and inorganic sublattices of HOIPs (and therefore the intrinsic non-radiative loss) by controlling the strength of cation-halide hydrogen bond or/and the rotational mobility of the cation, in agreement with some recent findings²⁴⁰. Consequently, our study offers a new design guideline to perovskite device optimization that may push the V_{oc} losses down to their radiative limit, significantly improving their photovoltaic performance.

IV. Conclusion

In conclusion, we have presented the first report of ultrafast vibrational control of a HOIP-based optoelectronic device. This experiment has provided access to the coupled electronic and structural dynamics of FAPbBr_3 metal halide perovskites, both as thin films and full optoelectronic devices. Our spectroscopic techniques, PC-VIPER and PL-VIPER spectroscopies, demonstrate that the $\nu(\text{N}=\text{C}=\text{N})$ stretching mode of FA can modulate the optoelectronic properties of the FAPbBr_3 . Analysis of the VIPER kinetics supports a picture in which coupling between the organic and inorganic sublattices results from a stochastic sticking and unsticking of the FA ion from the inorganic cage, mediated by cation-halide hydrogen bonding. Our results highlight the strongly dynamical nature of the coupling between the organic cation and the inorganic cage and establish a direct link between this coupling and the optoelectronic performance of hybrid perovskites. The observed phenomena are potentially responsible for the reduction of the intrinsic nonradiative recombination of HOIPs, which impacts their performance as solar absorbers. Importantly, we suggest that the degree of intrinsic non-radiative recombination can be controlled by optimizing the strength of hydrogen bond and cation mobility. In the future, vibrational control can be exploited to open new

functionalities in ultrafast optical switches for time-division multiplexed optical signals²⁴² as well as a powerful tool to study electron-phonon coupling, in both perovskites and a wider array of optoelectronic systems.

Part 5. Photoluminescent vibrationally-promoted electronic resonance spectroscopy of Rubrene single crystals

This part of the thesis presents novel, unpublished experimental results on the photoluminescence (PL) Vibrationally Promoted Electronic Resonance spectroscopy (VIPER) of high quality Rubrene single crystals. The discussion is addressing the ongoing debate in the literature on the role of symmetry breaking for singlet fission and the potential role of low-frequency vibrational modes in this process.

Abstract

Symmetry breaking is the cornerstone of many physical phenomena in particle physics, cosmology, chemistry and beyond. Recently, a novel concept in condensed matter physics has emerged – dynamic symmetry breaking (DSB). This phenomenon implies that symmetry in molecular single crystals may be broken via various intermolecular vibrations that may facilitate different processes, for example – singlet fission. However, at the moment it is difficult to name an experimental spectroscopic technique that is well suited for studying this fascinating phenomenon. In this work, we consider photoluminescence Vibrationally Promoted Electronic Resonance spectroscopy (PL VIPER) as such a technique. It is well suited for studying DSB because: (1) it is sensitive to electron-phonon interaction; (2) it has fs-time resolution, which will allow us to take into account the transient nature of this phenomenon; (3) it is sensitive to slow (low frequency) structural changes. Here we studied the PL VIPER of rubrene crystals in which DSB was predicted theoretically. Surprisingly, we discovered that despite highly symmetric C_{2h} structure, rubrene single crystals have some modes that are VIPER active in the fingerprint wavelength region. The characteristic lifetime of the VIPER signal (coinciding with the period of the theoretically predicted symmetry-

breaking mode), as well as the dependence of the VIPER intensity on temperature, support our hypothesis about the VIPER being caused by DSB. Our work potentially opens up new possibilities for using VIPER spectroscopy as a tool for studying dynamic symmetry breaking, as well as other processes associated with nonlocal electron-phonon interaction.

I. Introduction

The concept of symmetry is one of the most important for the modern understanding of the world – it stands at the cornerstone of the Standard Model of particle physics. According to the model, the Universe's existence in its present form is associated with spontaneous breaking of symmetry that led to the separation of weak nuclear and electromagnetic forces²⁴³.

Symmetry and symmetry breaking has been found to impact a vast range of phenomenon in chemistry, physics, and life sciences. The latter has been famously (and tragically) demonstrated by the example of thalidomide – the drug, which (S)-enantiomer harbours embryo-toxic and teratogenic effect that caused severe deformities among newborn children²⁴⁴. Symmetry plays a huge role in both condensed matter physics and laser spectroscopy. In condensed matter physics, the symmetry has been shown to influence many processes including charge carrier transport and phonons²⁴⁵, phase transitions²⁴⁶ and topological insulators²⁴⁷, quantum Hall effect^{247,248}, superconductivity²⁴⁹ and other magnetic phenomena.

In laser spectroscopy, molecular symmetry is notoriously known as a determiner of the selection rules for the optical transitions between various

excited states and intra-band transitions¹², and non-linear optical effects such as second harmonic generation²⁵⁰ and sum-frequency generation²⁵¹.

Recently, dynamic lattice symmetry breaking has been proposed as a mechanism facilitating singlet fission (SF) in rubrene single crystals¹⁴⁵. As has been mentioned in Part 1, Section 3.2, SF only occurs when there is a minimal mismatch between the energies of the singlet state and doubled energy of the triplet state:

$$E_{T1} \approx E_{S1}/2 \quad (5.1)$$

, where E_{T1} and E_{S1} are the energies of the triplet and singlet states correspondingly. However, the condition (5.1) alone is not sufficient to facilitate singlet fission. The intermolecular coupling plays an important role as well. In the diabatic treatment of the SF rate²⁵², this is defined by the matrix element:

$$V_{SF} = \langle S | H_{el} | (TT) \rangle \quad (5.2)$$

, where V_{SF} is the intermolecular coupling constant, which should be non-zero for the SF to occur⁹⁸ via the direct pathway²⁵³. There have been several studies showing rather sufficient values of intermolecular coupling V_{SF} in pentacene^{254,255}, yet in Rubrene V_{SF} has been found rather negligible due to face-to-face molecular stacking geometry with C_{2h} symmetry (see Ref. [145] for details).

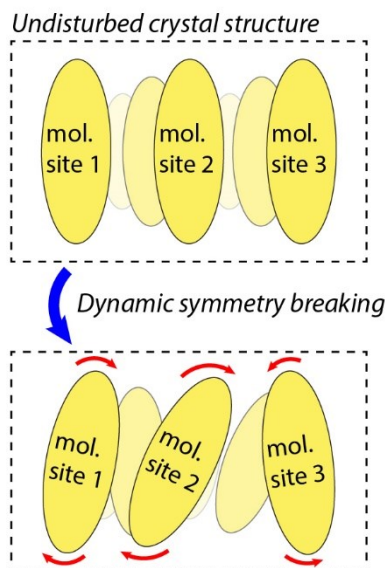


Figure 32. Dynamic symmetry breaking concept: breaking the perfect crystal structure symmetry via intermolecular modes may facilitate electronic processes such as SF.

To resolve this contradiction, Miyata¹⁴⁵ and others proposed the concept of the symmetry breaking (Figure 32) via an antisymmetric torsional mode. Such an intermolecular mode (see Part 1, Section II) may dynamically break perfect crystal structure and transiently improve V_{SF} . This concept was supported by DFT and QM/MM calculations, and the responsible mode was assigned as a torsional mode with tetracene backbone twisting along the long molecular axis at 124 cm^{-1} .

The work by Miyata has shown that the dynamic symmetry breaking (DSB) via intermolecular vibrations can control electronic processes (such as SF) in an

organic semiconductor. However, there are some disadvantages that should be highlighted:

- (1) The quantitative effect on SF (i.e., the prediction of the coherent yield of triplets) was not considered.
- (2) The model presented in the paper relies on the state-of-art complex DFT and QM/MM calculations, which may well be insufficiently accurate and method specific⁷⁵ (for example, additional modes can be involved in symmetry breaking, which were not taken into account).

The scepticism is corroborated by a recent report suggesting that instantaneous formation of triplets is related to defects and disorder⁸⁵. Though, it is assumed that defects may play a similar role in breaking crystal symmetry, but statically at defective sites. In this regard, even the very existence of dynamic symmetry breaking in Rubrene via intermolecular vibrations becomes questionable. However, at the moment, it is challenging to pinpoint any conventional spectroscopic technique (or other experimental method) that would have specificity to resolve this debate and validate previously suggested models.

In this work, we consider PL VIPER¹²⁸ spectroscopy as a promising candidate for probing dynamic symmetry breaking effects. VIPER is a mixed

vibrational/electronic spectroscopy, which makes it specifically sensitive to electron-phonon interaction. Furthermore, its temporal sensitivity to high-frequency couplings may reflect dynamic (low frequency $<200\text{cm}^{-1}$) structural changes as we showed in Part 4.

In this work, we used PL VIPER spectroscopy to measure Rubrene single crystals that has been predicted earlier to have DSB. We found that despite highly symmetrical orthorhombic structure (C_{2h} symmetry group with centre of inversion), there are some VIPER-active modes in the fingerprint wavelength region. The VIPER signal was identified to have short lifetime that we associated with the symmetry breaking effect induced via a low-frequency mode. Our hypothesis is supported by characteristic lifetime of the VIPER signal ($\sim 240\text{fs}$) (coinciding with the period of the theoretically predicted symmetry-breaking mode), and VIPER intensity dependence on temperature. Furthermore, at low temperatures ($<200\text{K}$) we identified a long-lived VIPER signal at unexpected frequency of 1700cm^{-1} . There are no modes of Rubrene at this frequency, and we attributed this signal to some small concentration of Rubrene double oxide impurities incorporated in the crystal at low temperature. The signal has a lifetime much longer than previously found one, and this we associate with the absence of inversion symmetry of the Rubrene double oxide molecules²⁵⁶.

II. Experimental section

In this study, we used the VIPER spectroscopy setup, which was already described in Part 2 of this thesis. In the case of rubrene single crystals, the visible excitation (VIS) wavelength was selected at 600 nm, obtained by second harmonic generation of the 1200 nm signal beam from the TOPAS parametric light amplifier (Coherent) with a BBO nonlinear crystal.

Figure 33a shows arrangement of VIS excitation relative to Rubrene absorption, as well as a Rubrene single crystal PL spectra and PL detection window used in the experiments. For middle infrared (MIR) pre-excitation of vibrations, the central pulse wavelength was selected at 1500 cm^{-1} to cover the organic molecules fingerprint region (from approx. 1300 cm^{-1} to 1800 cm^{-1} , Figure 33b). Figure 33c conveniently summarizes the main experimental parameters with the experimental VIPER schematic.

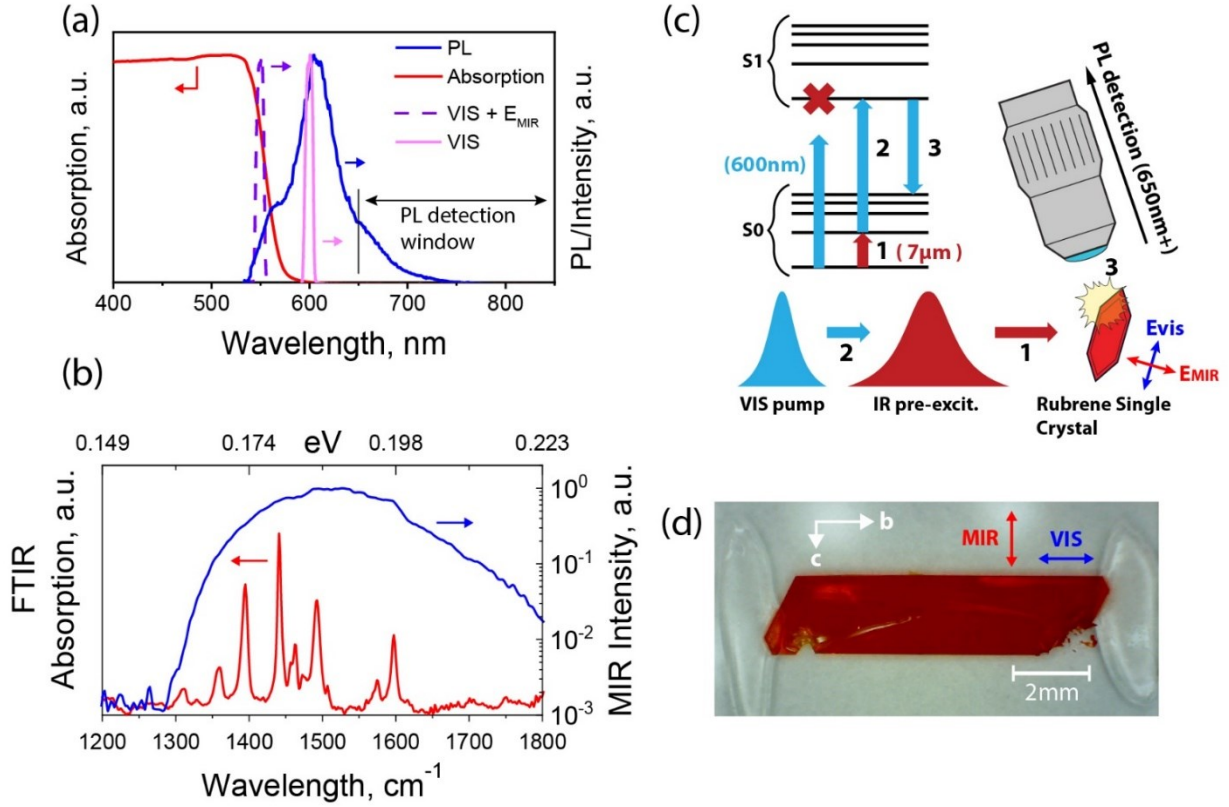


Figure 33. Experimental parameters for PL VIPER spectroscopy of Rubrene single crystals. (a) Absorption spectrum of a thick Rubrene single crystal and visible excitation spectrum (dashed line is with added MIR pulse energy); Rubrene photoluminescence spectrum and PL detection window. (b) MIR pre-excitation spectra and Rubrene FTIR absorption spectra. (c) PL VIPER experiment schematic for Rubrene single crystals. (d) Optical microscopy image of the measured Rubrene single crystal.

In this study, we used Rubrene single crystals described in Part 3 (PVT purified 4-5 times to minimize impurity concentrations^{56,117}, Figure 33d). Both IR and VIS beams were directed orthogonally to the 0bc crystal plane: $\vec{k}_{VIS}, \vec{k}_{MIR} \perp 0bc$,

$\vec{E}_{VIS}, \vec{E}_{MIR} \parallel 0bc$. To minimize the coherent effects (such as sum frequency generation), MIR and VIS beams were orthogonally polarized: $\vec{E}_{VIS} \perp \vec{E}_{MIR}$ (see MIR beam polarization survey in Appendix E). The VIS beam polarization was directed along the 0b long axis of the crystal (Figure 33d).

The power of both beams was chosen to maximize the signal-to-noise ratio without causing sample degradation. In these experiments, the powers were $P_{VIS} = 100\mu W$ for visible beam measured before the 10cm focusing silver mirror (focusing spot on samples $\sim 200\mu m$), and $P_{MIR} = 4mW$ measured in the same place under dry air conditions at the interferometer time zero. All experiments were conducted with dry air purging the experimental setup. For temperature control, we used HFS600E-PB4 Linkam stage.

III. Results

Figure 34 provides a summary of the experimental PL VIPER data obtained for rubrene single crystals: (a, b) show 2D PL VIPER maps for different temperatures, (c, e) show the kinetics of the most prominent VIPER-active peaks.

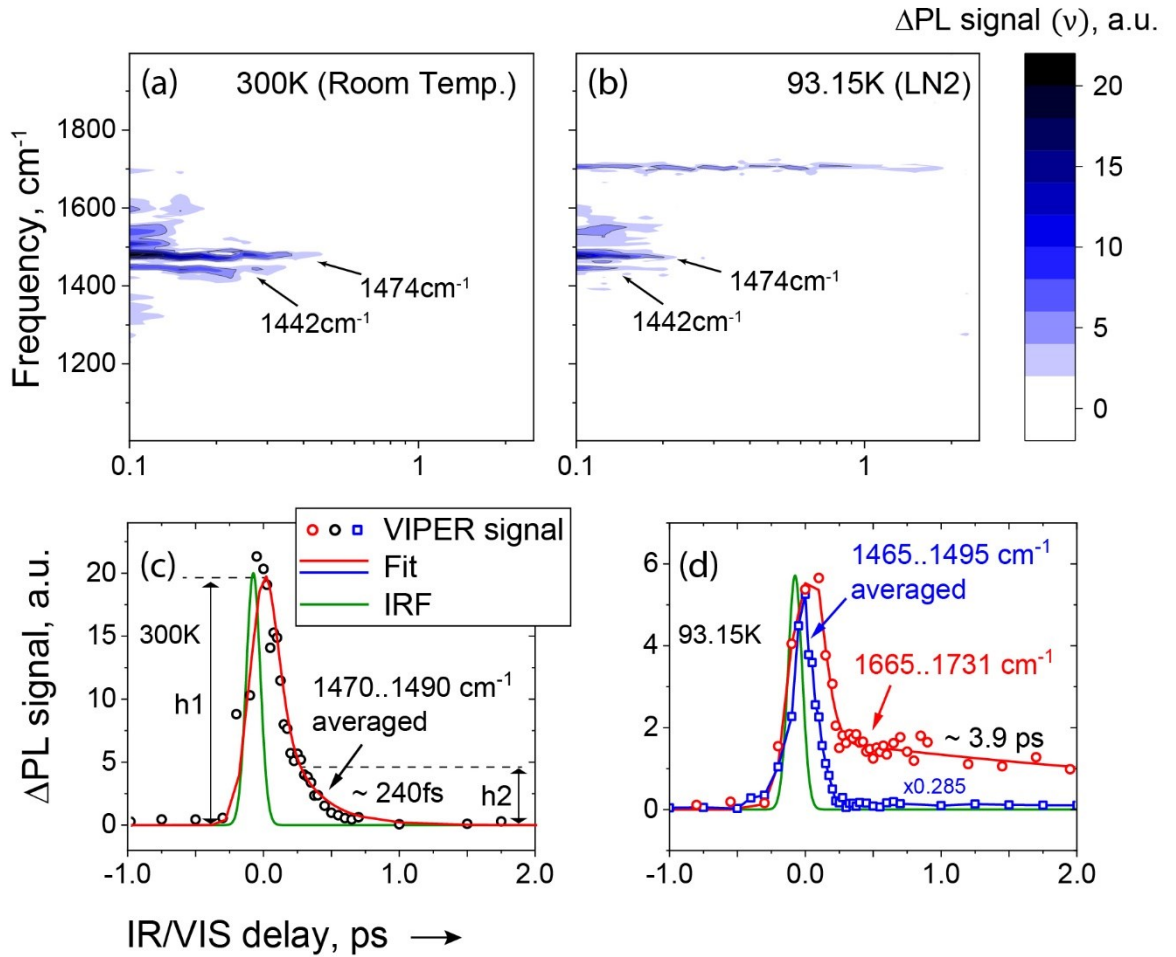


Figure 34. PL VIPER spectroscopy of Rubrene single crystals. (a, b) Frequency resolved 2D map as a function of MIR frequency and VIS/IR pulses delay at 300K

(a) and at 93.15K (b). PL VIPER kinetics at 300K (c) and at 93.15K (d). Scatter plots are experimental data; lines are fits.

When measured at room temperature (300K) and when MIR precedes VIS pulses, a short-lived signal, similar to what was previously seen for metal-organic perovskites (see Chapter 4), was observed (Figure 34, a). The signal is distinctively of VIPER nature, because of the well spectrally resolved narrow peaks coinciding with the Rubrene FTIR absorption peaks, and quite significant lifetime of the signal longer than the instrument response function (IRF) (~ 100 fs) (Figure 34, c). The most pronounced VIPER-active modes were found to be 1474 cm^{-1} and 1442 cm^{-1} (Figure 34, a).

The VIPER signal at 1474 cm^{-1} and 1442 cm^{-1} has a similar lifetime and can therefore be characterized by the same kinetics. Figure 34c shows the kinetics for the 1474 cm^{-1} mode. Evidently, the VIPER signal is very short-lived (< 1 ps, which is significantly shorter than the expected vibrational lifetime; see Part 4, Sections II and III), but it still greatly exceeds the duration of the instrument response function (IRF). To extract the VIPER signal lifetime, an approximation was made using the bi-exponential decay function convoluted with a Gaussian. A faster exponential characterizes the process around time zero, which is most likely dominated by coherent processes (such as sum-frequency generation of VIS and

MIR pulses) to some extent. On the contrary, the decay time of the slower exponential should precisely characterize the lifetime of the VIPER signal. In the fit presented in Figure 34c, the lifetime of the VIPER signal was determined to be 240 ± 8 fs.

After decreasing the temperature of the Rubrene single crystal down to 93K, 2D Δ PL VIPER map changes significantly Figure 34b. The previously observed peaks at 1474 cm^{-1} and 1442 cm^{-1} become less pronounced, which may be due to the decrease of VIPER activity of these modes. Surprisingly, at 1700 cm^{-1} a completely new mode appears, which is distinguished by a huge (compared to other observed modes) lifetime ($>2\text{ps}$). Figure 34d shows the kinetics of the 1700 cm^{-1} at 93K, as well as a bi-exponential fit. The 1700cm^{-1} mode lifetime was determined as 3.9 ± 0.8 ps.

Figure 35a compares the PL VIPER spectra at 300K and 90K with the FTIR and Raman measured at room temperature. The VIPER active modes, which are observed at 300K ($1442, 1474, 1508\text{ cm}^{-1}$), are clearly visible at 90K as well. Clearly, the modes observed in PL VIPER signal coincide with the corresponding IR active modes. However, there is no clear coincidence of these modes with the peaks in the Raman spectrum. In addition, the mode at 1700 cm^{-1} , which is activated at low temperature, is absent in both the FTIR and Raman spectra of Rubrene.

Figure 35b,c present the above-mentioned PL VIPER observations in a quantitative manner. The amplitude of the 240-fs signal at 1442, 1474, 1508 cm^{-1} decreases greatly with decreasing temperature, almost reaching zero at 93 K. The long-lived Viper signal at 1700 cm^{-1} is activated at approximately 200K (Figure 35, c).

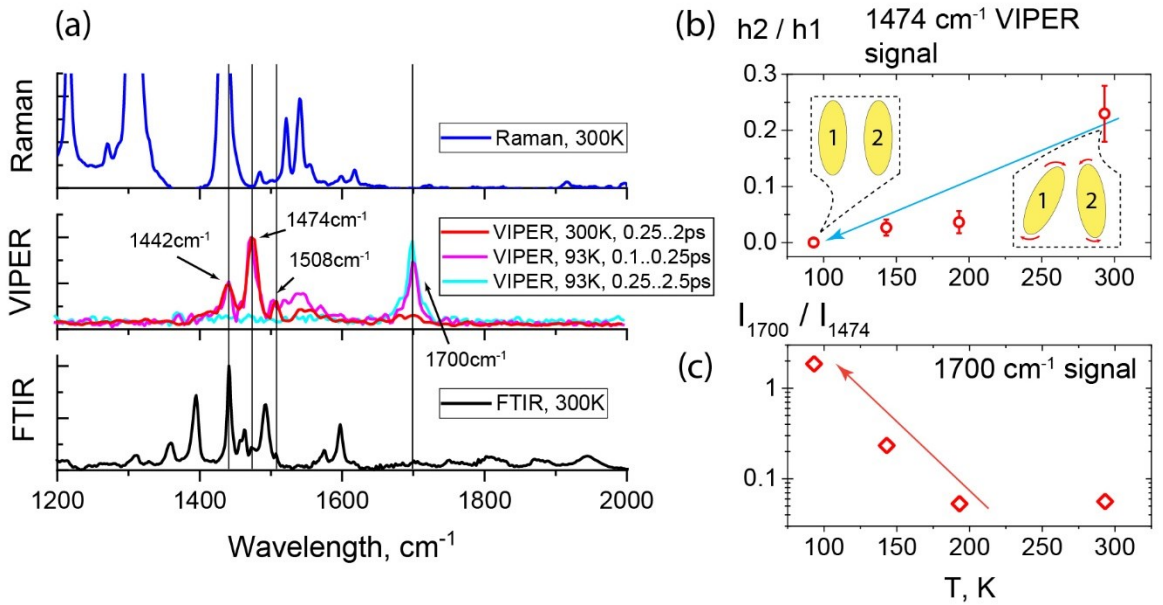


Figure 35. (a) Comparison of PL VIPER spectra measured at different temperatures with Raman spectra of a Rubrene single crystal (measured with 633nm excitation laser, polarization || oB) and FTIR spectra of the evaporated Rubrene film. (b) Intensity of the VIPER-active mode 1474 cm^{-1} (extracted from kinetics fit, assuming the same exponential decay times) versus temperature. Insets schematically show decrease of symmetry breaking via intermolecular modes with temperature decrease. (c) Relative intensity of the VIPER mode 1700 cm^{-1} versus temperature (extracted from spectra averaged from 0.1 to 2.5 ps VIS/IR delay).

IV. Discussion

First, let us address the conditions allowing PL VIPER activity of vibrational modes. Previously, it has been shown that vibrational modes, which are both IR and Raman active, are allowed for the VIPER process and have quite considerable VIPER activity¹³¹. Such a scenario of simultaneous IR/Raman activity is only possible in the absence of inversion symmetry, such as in the FA⁺ cation in perovskites (see Part 4). Since there is a centre of symmetry in the Rubrene single crystal as well (C_{2h} point group), it would be logical to assume that there should be no VIPER active modes in an ideal Rubrene single crystal. Nevertheless in this work we found the short-lived VIPER signal from some of the fingerprint IR active modes of Rubrene.

The presence of such short-lived VIPER signal may be explained in the framework of dynamic symmetry breaking. It is very well known that the intermolecular vibrations are populated at room temperature and disturb an ideal energetic landscape of the crystal. Similarly to introducing “dynamic disorder” into the energetic landscape⁷³, low frequency vibrations may introduce transient symmetry breaking at various molecular sites of the crystal. Therefore, we assume that the observation of the short-lived VIPER signal in the 1400-1520 cm⁻¹ region

is associated with such molecular sites with transiently broken symmetry of inversion.

This hypothesis can help to explain the short lifetime of the PL VIPER signal as well. The breaking of symmetry is transient in nature, therefore the time of the VIPER activity of the pre-excited molecular site can be estimated as period of the symmetry breaking mode: $\tau_{VIPER} \approx T_{LF}$, where T_{LF} is the period of the intermolecular vibration, and τ_{VIPER} is the lifetime of the Viper signal. With this in mind, we can estimate the frequency of the symmetry-breaking vibrational mode simply as: $\omega_{LF} \approx 1/\tau_{VIPER}$. Extracting the lifetime of τ_{VIPER} from the kinetics (240 ± 8 fs, Figure 34c), we obtain the characteristic frequency of the symmetry-breaking mode of $139 \pm 10\text{cm}^{-1}$. Fascinatingly, this perfectly agrees with the frequency of the theoretically-predicted symmetry-breaking mode reported earlier¹⁴⁵.

The hypothesis of the VIPER-activity being related to dynamic symmetry breaking is strongly corroborated by the temperature-dependent measurements (Figure 34; Figure 35, b-c). The effects of dynamic symmetry breaking should decrease with decreasing temperature, as low-frequency vibrational modes would depopulate. If our assumption about the connection between the PL VIPER signal and the dynamic breaking of symmetry is correct, then the intensity of the PL

VIPER signal should also decrease with lowering temperature. This is exactly what is observed in the experiments (Figure 35, b).

Now we address the question of the emergence of a new long-lived VIPER mode at 1700 cm^{-1} at low temperatures. As can be seen in the Figure 35a, this mode is not observed in either the FTIR or Raman spectra of Rubrene. What kind of mode is this and why is it activated in the PL VIPER signal? From the literature analysis, we found that the modes at 1700 cm^{-1} may originate from vibrations of the C=O chemical bond. Indeed, there were reports on the oxidization of Rubrene molecules in ambient atmosphere^{256,257}. It has also been shown that rubrene oxide is always located on the surface of single crystals and can penetrate to depth with the strong photo-induced degradation²⁵⁷.

To verify that the 1700 cm^{-1} mode originates from the oxidized molecules of Rubrene, we prepared solutions of rubrene oxides according to the procedure described in [256]. Films were then prepared from these solutions and PL VIPER maps were measured (Table 1, concentration and preparation details are identical to [256]). It was found that exactly the same long-lived signal at 1700 cm^{-1} is observed when measuring a film of rubrene double oxide (Figure 36), which suggests that the origin of this mode is the Rubrene oxidized molecules incorporated in Rubrene single crystals.

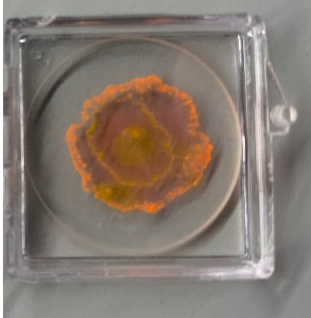
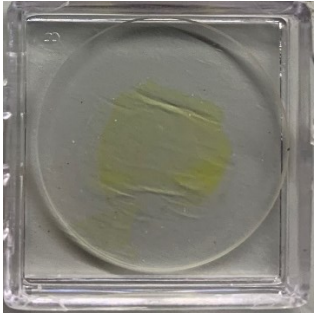
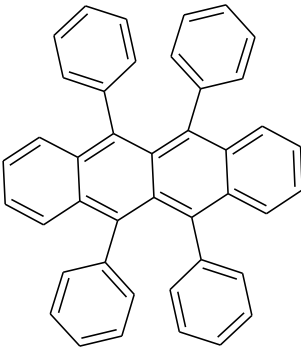
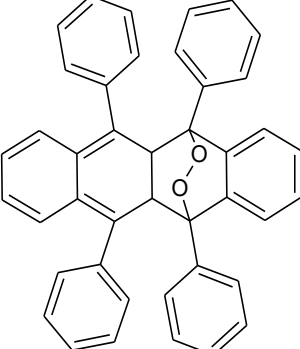
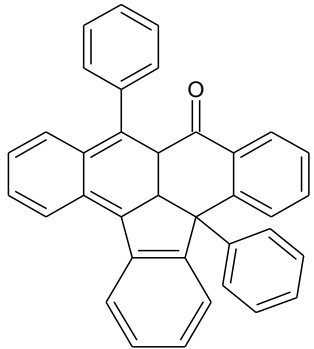
a) Rubrene film	b) Rubrene oxide film	c) Rubrene double oxide film
		
Deposited from chloroform solution (>10mg/ml)	Deposited from 2-days old chloroform solution kept in ambient conditions	Deposited from 4-weeks old chloroform solution kept in ambient conditions
		

Table 1. Rubrene oxidization products, rows: film images, preparation details and structural formulas. (a) Rubrene. (b) Rubrene single oxide. (c) Rubrene double oxide.

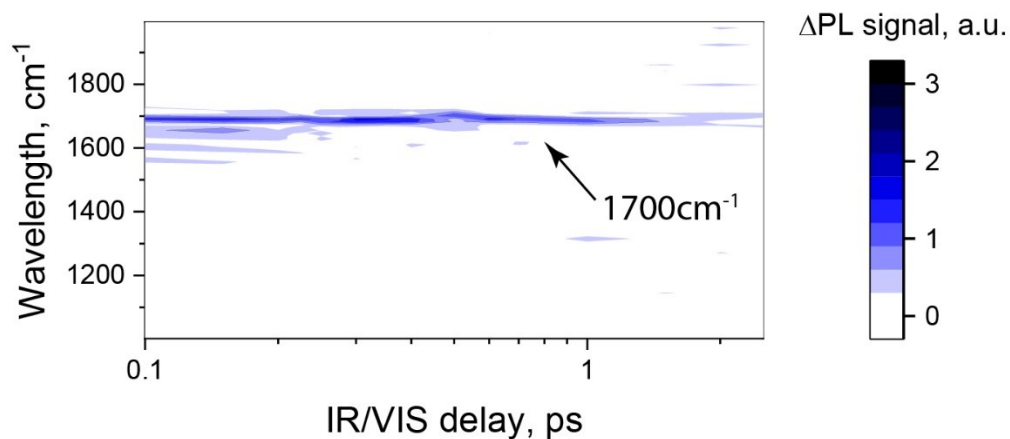


Figure 36. 2D PL VIPER map of Rubrene double oxide film. VIS excitation pulses: 200uW at 450nm; IR pre-excitation pulses: centred at 1700cm^{-1} , $\sim 3\text{mW}$ IR power.

It can be assumed that the molecules of rubrene double oxide penetrate through the surface of rubrene single crystals in a certain way during cooling, for example, through cracks on the surface and are embedded in the crystal lattice, thus increasing the static disorder in the system. This assumption agrees well with the recent reports on the structural deformation of Rubrene crystals at temperatures below 200K ²⁵⁸. Moreover, the increased role of the static disorder is a generally very well-known phenomenon for organic single crystals, which negatively affects performance of transistors based on high mobility single crystals at low temperatures. However, previously, the exact mechanism of the defects formation at low temperatures was insufficiently studied.

Excitingly, VIPER spectroscopy turned out to be extremely sensitive to what appears to be a very subtle effect of the formation of oxide defects at low temperatures. This can be attributed to the specific selection rules in the VIPER process: simultaneous IR and Raman activity was found to be the best case for the maximum VIPER activity of vibrational modes.

For regular single crystal of Rubrene, which has an inversion center, this process is possible only with dynamic symmetry breaking. However, Rubrene double oxide molecule lacks an inversion center, so the 1700 cm^{-1} vibrational mode is always IR and Raman active. Therefore, the VIPER process will occur with higher probability on double oxide molecules and, importantly, would not be limited in time via intermolecular interactions. This is confirmed with experimental observation of the long lifetime of the VIPER signal of 1700 cm^{-1} mode ($3.9 \pm 0.8\text{ps}$, Figure 34, d).

These experimental findings pave the way for the new application of VIPER spectroscopy: detection low concentrations of impurities in systems of center-symmetric molecules.

V. Conclusion

In this work, we presented the results of PL VIPER spectroscopy of Rubrene single crystals. Our results indicate that the VIPER activity in rubrene single crystals is associated with symmetry breaking via intermolecular vibrations — dynamic symmetry breaking effect. This hypothesis is supported by the short lifetime of the VIPER signal, which coincides with the period of the symmetry-breaking vibrational mode previously predicted theoretically. As well as deactivation of the PL VIPER signal with deactivation of intermolecular vibrations at low temperatures. In addition, the long-lived signal from oxidized rubrene molecules (without an inversion center) at low temperature was discovered. Apparently, the concentration of these impurity molecules is very low as they could not be detected by conventional spectroscopic techniques, such as FTIR and RAMAN.

These experimental results open new horizons for the application of VIPER spectroscopy. PL VIPER can be used as a tool for elucidating dynamic symmetry breaking in centrosymmetric materials, as well as finding low concentrations of impurity molecules.

We have shown that PL VIPER spectroscopy has unique advantages that often help to overcome the limitations of conventional spectroscopies. Undoubtedly, PL

VIPER spectroscopy has an enormous potential for studying and monitoring the effects of electron-phonon interactions that can facilitate the development of more efficient semiconducting materials.

Part 6. Conclusions and future work

This thesis was devoted to elucidating some of the open question in the field of soft organic and hybrid semiconductors. To achieve this, we used a range of modern ultrafast spectroscopy techniques, such as Transient Absorption Spectroscopy (TAS), and developed a new technique called Photoluminescence Vibrationally Promoted Electronic Resonance spectroscopy (PL VIPER). The special attention was given to studying the role of vibrations and electron-phonon interaction for excitation dynamics in the studied phenomena.

Conventionally, the prevailing opinion in the literature is about the negative role of electron-phonon interaction for soft (organic and hybrid) optoelectronics^{38,73}. Undoubtedly, it plays a negative role in many processes, especially for charge transport, as we emphasized in the introduction (see Part 1, Section 2.2). However, in this work, we showed that it can also play a positive role for some other phenomena. For example, as we showed in Part 3, electron-phonon interaction plays a central role in promoting the phenomenon of singlet fission, which is proposed to be used to improve the efficiency of solar cells. In addition, as we showed in Part 4, HF electron-phonon couplings can be used to

study the dynamic structural changes in a material. For example, the kinetics of the VIPER signal of the HF mode 1720 cm^{-1} indicates the dynamic re-orientation of the organic cation inside the perovskite.

In this thesis, we aimed to answer the following questions:

- 1) Does the formation of mixed states occur during the process of singlet fission in Rubrene single crystals? What is the role of molecular vibrations in this process? (Part 3)
- 2) How organic and inorganic sublattices are coupled in organohalide perovskites? Can this be important for their optoelectronic properties? (Part 4)
- 3) Does dynamic symmetry breaking occur in rubrene crystals? (Part 5)

In this chapter, we will summarize the conclusions to each of these questions with our results in mind. Additionally, we will suggest new possible directions for further exploring the researched topics.

I. Ultrafast singlet fission dynamics in Rubrene single crystals

In this part of the thesis, we used multi-timescale TA spectroscopy to investigate singlet fission (SF) dynamics in high-purity Rubrene single crystals. This

system has recently attracted a lot of attention due to some contradictory reports on the physics of the triplet excitons formation. This was the main driver of our research.

We have indeed found that triplet formation is mediated with the mixed singlet-triplet multiexciton state [S:TT] as we initially suspected. Moreover, we found that [S:TT] is the initially photoexcited state, which quickly transitions into either a pure singlet state S or a T+T triplet pair within about 80 fs. Subsequently, the pure singlet state may undergo conventional temperature-activated SF, but at much slower 10 ps rate. As the modelling shows, the mixed state is characterized as a vibronically-enhanced mixture of the S and TT multiexciton states.

Our results potentially reconciles varying models of singlet fission in crystalline rubrene. Coherent SF is occurring immediately after photoexcitation, as highlighted for example by Miyata et al.¹⁴⁵, and the incoherent (hopping-like) SF is taking place over a potential energy barrier via thermal activation. Additionally, our study demonstrated that the SF pathway can be controlled with the choice of excitation photon energy.

Potential future work may involve (1) exploring different molecular design aspects to enhance control over the fission mechanism and advance the

development of SF-enhanced photovoltaic materials; (2) explore the anisotropy-related effects, as this can be important degree of freedom affecting both incoherent and coherent SF pathways; (3) to study in detail the effect of the single crystals degradation on the SF rate of both coherent and incoherent pathways.

II. Role of organic cation in organohalide perovskites

In this part of the thesis, we presented the first report of the ultrafast vibrational control of hybrid organic-inorganic perovskites (HOIP). The novel PL-VIPER spectroscopy (as well as PC-VIPER) has allowed us to access the coupled electronic and structural dynamics of FAPbBr₃ metal halide perovskites.

This powerful experimental technique has allowed us to experimentally identify the coupling of inorganic and organic sublattices: $\nu(\text{N-C=N})$ stretching mode of FA can modulate the optoelectronic properties of the FAPbBr₃ perovskite. Moreover, our kinetics analysis (in conjunction with modelling) supports the dynamic picture of stochastic sticking and unsticking of the FA⁺ cation from the inorganic cage, mediated by cation-halide hydrogen bonding. The observed phenomenon can potentially be responsible for the reduction of the intrinsic nonradiative recombination of HOIPs, which impacts their performance as solar absorbers (see Part 4, Section IV).

This work has highlighted distinctive advantages of PL VIPER spectroscopy as a tool for studying electron-phonon interactions in complex materials consisting of several components (in the case of HOIP: organic and inorganic sublattices).

We suggest that by optimizing the strength of hydrogen bond and cation mobility, it can be potentially possible to control the intrinsic non-radiative losses in perovskites solar cells. Therefore, the potential future work may involve stronger material aspect, for example, (1) correlating strength of cation-halide bonding and non-radiative losses in a series of perovskites with different organic cations and halides. Further, we plan to use PL VIPER spectroscopy for studying other types of PV semiconductors, for example, (2) 2D perovskites and (3) organic bulk-heterojunction blends.

III. Photoluminescent vibrationally-promoted electronic resonance spectroscopy of organic single crystals

This part of the thesis presented the results of PL VIPER spectroscopy of Rubrene Single crystals. Our interest in applying VIPER spectroscopy to single component, highly symmetrical system such as Rubrene was inspired by our previous PL VIPER HOIP results. In Part 4, we revealed that the high-frequency ($>1000\text{cm}^{-1}$) modes pre-excited in PL VIPER may reflect slower dynamic (low frequency $<200\text{cm}^{-1}$) structural changes within the material. Similar effects has

been previously proposed to control optoelectronic properties in organic single crystals. In particular in relation to charge transfer (transient localisation) and singlet fission (dynamic symmetry breaking). Yet, there were significant lack of experimental tools to support these ideas.

In this chapter we have successfully used PL VIPER spectroscopy as a tool for probing such effects. Despite the highly symmetrical structure of Rubrene single crystals, which does not imply strong VIPER activity of vibrational modes, we nevertheless were able to detect some short-lived VIPER signal.

Our findings suggest that the VIPER activity observed in rubrene single crystals is linked to symmetry breaking caused by intermolecular vibrations, indicating a dynamic symmetry-breaking effect. This hypothesis gains support from the brief lifespan of the VIPER signal, aligning with the expected period of theoretically predicted symmetry-breaking vibrational modes. Moreover, the deactivation of the PL VIPER signal correlates with the deactivation of intermolecular vibrations at low temperatures. Notably, we identified a long-lived signal (at 1700 cm^{-1}) most likely arising from oxidized rubrene molecules at low temperature ($<200\text{ K}$). Evidently, the concentration of these impurity molecules is exceedingly low, as it was undetected by conventional spectroscopic techniques such as FTIR and RAMAN.

These experimental findings unveil exciting possibilities for the utilization of VIPER spectroscopy. PL VIPER emerges as a valuable tool, offering insights into dynamic symmetry breaking in centrosymmetric materials and enabling the detection of low concentrations of impurity molecules. This opens up new horizons for the application of PL VIPER in diverse research areas.

Further, we plan to study in detail the mechanisms of the 1700 cm^{-1} mode activation: (1) conduct additional experiments with the temperature dependence of the IR and Raman spectra of pure rubrene single crystals, (2) rubrene double oxide films and ordinary Rubrene films. (3) Finally, we plan to support our experimental PL VIPER results with theoretical models and density functional theory (DFT) calculations.

Appendix A. Application of Hückel model

In this section the Hückel model is used to calculate HOMO/LUMO energy splitting in the ethylene molecule and the corresponding wavefunctions. The Hückel model is an approximate model used for the π -conjugated systems. The approximations are listed below¹²:

1. The σ - and π - bonding orbitals are separated into two independent subsystems (frameworks). This is often referred as “sigma-pi” separability and is justified by the orthogonality of σ - and π - orbitals.
2. The σ bonds has already been formed in the molecule and serve as a rigid backbone.
3. Only the formation (energies and shapes) of π -orbitals is considered.
4. The π - orbitals expressed as linear combination of carbon $2p_z$ orbitals (Linear combination of atomic orbitals LCAO).
5. All C atoms are treated as being identical.
6. All coulomb integrals are: $H_{ii} = \alpha$.
7. All resonance integrals between adjacent C atoms are: $H_{ij} = \beta$.

8. All other resonance integrals (between not adjacent atoms) are equal to zero.

9. All overlap integrals are equal to zero: $S_{ij} = 0$.

We start with representing the ethylene molecular orbitals as a linear combination of the $2p_z$ carbon orbitals:

$$|\psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \quad (\text{A. 1})$$

,where $|\phi_1\rangle$ and $|\phi_2\rangle$ are atomic orbitals of adjacent carbons, and c_1 and c_2 are numerical coefficients.

By substituting (A. 1) into the stationary Schrödinger equation:

$$\hat{H}|\psi_i\rangle = E|\psi_i\rangle \quad (\text{A. 2})$$

,we arrive at the following expression:

$$\hat{H}c_1|\phi_1\rangle + \hat{H}c_2|\phi_2\rangle = Ec_1|\phi_1\rangle + Ec_2|\phi_2\rangle. \quad (\text{A. 3})$$

Now by simply multiplying (A. 3) from the left by $\langle\phi_1|$ and separately by $\langle\phi_2|$, we will obtain the system of equations for finding the ethylene energy levels:

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (\text{A. 4})$$

,where

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \quad (\text{A. 5})$$

$$S_{ij} = \langle \phi_i | \phi_j \rangle \quad (\text{A. 6})$$

This system (A. 4) has a non-trivial solution (the trivial one is: $c_1 = c_2 = 0$),
when:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (\text{A. 7})$$

,which expands into the following expression:

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})(H_{21} - ES_{21}) = 0. \quad (\text{A. 8})$$

Taking into account the assumptions (6 – 9) of the Hückel model (see above),
we finally get the expression for the Energy levels of the π -orbitals in ethylene:

$$(E - \alpha)^2 - \beta^2 = 0 \quad (\text{A. 9})$$

,or

$$E_{\pi/\pi^*} = \alpha \mp \beta. \quad (\text{A. 10})$$

In equations (A. 9) and (A. 10), we used the notation $H_{ii} = \alpha$, $H_{ij} = \beta$, and set all the overlap integrals $S_{ij} = 0$.

With the discovered energy values, the corresponding π - and π^* -ethylene wavefunctions can be found with ease. For this, the coefficients c_1 and c_2 in (A. 1) should be determined. This can be done by inserting energies (A. 10) to the system of equations (A. 4) and dividing the whole system by β .

After the abovementioned procedure for the bonding π -orbital we get:

$$\begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (\text{A. 11})$$

, which gives $c_1 = c_2$ and the wavefunction attributed to this energy ($E_{\pi} = \alpha + \beta$; $\beta < 0$) is then:

$$|\psi_1\rangle = N_1(|\phi_1\rangle + |\phi_2\rangle) \quad (\text{A. 12})$$

Similarly, for the anti-bonding π^* -orbital ($E_{\pi} = \alpha - \beta$; $\beta < 0$) we get:

$$\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \times \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad (\text{A. 13})$$

, which gives $c_1 = -c_2$ and the corresponding wavefunction is then:

$$|\psi_2\rangle = N_2(|\phi_1\rangle - |\phi_2\rangle). \quad (\text{A. 14})$$

The N_1 and N_2 coefficients can be simply found via the standard normalization approach, (taking into account $\langle\psi_i|\psi_i\rangle = 1$):

$$N_1 = N_2 = 1/\sqrt{2}. \quad (\text{A. 15})$$

Appendix B. Basic properties of creation and annihilation operators

$a^\dagger$ — creation operator.

a — annihilation operator.

The creation and annihilation operators have outstanding properties when operating on Fock states — states with a precisely defined number of particles²⁵⁹.

If there are n particles in the Fock state $|n\rangle$, where n is an integer, then the following relations take place:

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad (B. 1)$$

$$a |n\rangle = \sqrt{n} |n-1\rangle \quad (B. 2)$$

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle \quad (B. 3)$$

Using the above relations (B. 1)-(B. 2), the number operator N can be defined:

$$N = a^\dagger a \quad (B. 4)$$

$$N |n\rangle = n |n\rangle. \quad (B. 5)$$

In addition, the following commutation relations take place:

$$[a, a^\dagger] = 1 \qquad (B. 6)$$

$$[N, a^\dagger] = a^\dagger \qquad (B. 7)$$

$$[N, a] = -a. \qquad (B. 8)$$

Appendix C. Supporting information for Part 3

I. Matching the crystal axis orientation with the shape of the rubrene single crystal

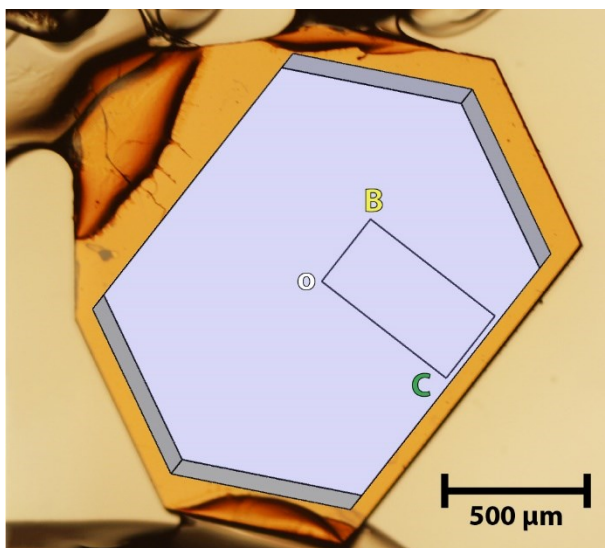


Fig. C1. Assignment of the single crystal habitus to unit cell orientation. Background – a rubrene single crystal microscopy image. Foreground – habitus model and corresponding orientations of the unit cell axes calculated with the Morphology module of the Material Studio package²⁶⁰ (Compass force field)²⁶¹.

II. Computational details

This part describes the basic computational details for Part 3. Full details can be found in [133].

1.1 Thermally-activated SF rate calculations

The ground state (G) geometry of the rubrene molecule underwent optimization at the density functional theory (DFT) level using the B3LYP functional and 6-31G(d,p) basis set. In addition, harmonic vibrational frequencies were computed for the energy-minimized structure to verify the absence of imaginary frequencies. Subsequent time-dependent DFT (TD-DFT) calculations were conducted to optimize the geometries of the first singlet (S) and triplet (T) excited states. For the $G \rightarrow T$ and $S \rightarrow T$ transitions, Huang-Rhys (HR) factors were calculated between relevant states. The complete list of computed factors can be found in Tables S2-S4 at [133]. The DFT calculations were executed using the Gaussian 16 package 7.

The transition rate constant (k) for the $S \rightarrow TT$ transition was estimated within the Marcus-Levich-Jortner model:

$$k = \frac{2\pi}{\hbar} t^2 \times \frac{1}{\sqrt{4\pi\lambda_c k_B T}} \sum_{n=0}^{\infty} \frac{e^{-S_{qm}} \times S_{qm}^n}{n!} e^{\frac{-(\Delta E + \lambda_c + n\hbar\omega_{qm})^2}{4\lambda_c k_B T}} \quad (C. 1)$$

, where t denotes electronic coupling; k_B is the Boltzmann constant; ΔE is the energy difference between $G + S$ and $T + T$ states; λ_c is the classical reorganization energy with low frequency modes (i.e., $<100 \text{ cm}^{-1}$); $\hbar\omega_{qm}$, the vibration energy of the effective high-frequency quantum mode; and S_{qm} , the Huang-Rhys factor associated with the reorganization energy from high-frequency modes.

The ω_{qm} and S_{qm} were determined as follows:

$$\omega_{qm} = \sqrt{\frac{(\sum \lambda_i \omega_i^2)_{S_0 \rightarrow T_1} + (\sum \lambda_i \omega_i^2)_{S_1 \rightarrow T_1}}{(\sum \lambda_i)_{S_0 \rightarrow T_1} + (\sum \lambda_i)_{S_1 \rightarrow T_1}}} \quad (C. 2)$$

$$\lambda_{qm} = \hbar\omega_{qm}S_{qm} \quad (C. 3)$$

, where ω_i and λ_i represent the frequency and reorganization energy associated with mode i , respectively. Rate calculations were conducted over the experimental temperature range of 125K to 330K. Energies for the S and T states, derived from reported experimental data, were assigned as 2.23 eV and 1.14 eV, resulting in a ΔE value of 0.05 eV. The vibrational modes with frequencies below 100 cm^{-1} were treated classically, while those with frequencies exceeding 100

cm^{-1} were treated quantum-mechanically. This yields $\omega_{qm} = 1368 \text{ cm}^{-1}$, $\lambda_c = 185 \text{ cm}^{-1}$, and $S_{qm} = 1.64$. To take into account the surrounding medium effects and crystal lattice relaxations, we added additional 0.1 eV to λ_c .

The activation energy (E_a) was determined by plotting the natural logarithm of the SF rate $\ln(k)$ against $k_B T$ (Fig. C2). The E_a was found to be 49.4 meV (52.2 if the environmental effects and crystal lattice relaxations are taken into account).

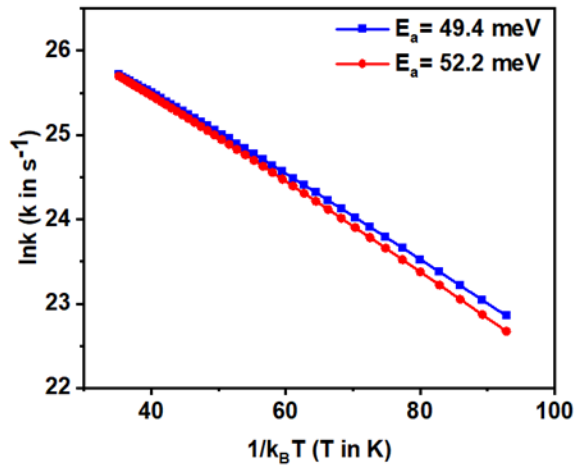


Fig. C2. Rate constants (k) as a function of inverse temperature (T) between 125 K and 330 K. The blue line is generated by adding 0.1 eV to λ_c to incorporate the effects of the medium and crystal lattice relaxations, while the red line does not consider such effects.

The S:TT coupling was simulated via a 3-state model of interacting singlet (S), triplet (T) and TT states:

$$H_{vib} = \begin{pmatrix} E_G + H_{vib}^{(G)} & -(\vec{d}\vec{E}) & 0 \\ -(\vec{d}\vec{E}) & E_S + H_{vib}^{(S)} & t \\ 0 & t & E_{TT} + H_{vib}^{(TT)} \end{pmatrix} \quad (C. 4)$$

$$H_{vib}^{(G)} = \sum_i \frac{\hbar\omega_i}{2} q_i^2 \quad (C. 5)$$

$$H_{vib}^{(S)} = \sum_i \frac{\hbar\omega_i}{2} q_i^2 + \sum_i \sqrt{2} \hbar\omega_i g_i^{(S)} + \lambda_s \quad (C. 6)$$

$$H_{vib}^{(TT)} = \sum_i \frac{\hbar\omega_i}{2} q_i^2 + \sum_i \sqrt{2} \hbar\omega_i g_i^{(TT)} + \lambda_{TT} \quad (C. 7)$$

$$\lambda = \sum_i \hbar\omega_i g_i^2 \quad (C. 8)$$

,where E_G is the energy of the ground state, E_S is the energy of the singlet state, and E_{TT} is the energy of the TT state. The variable t denotes the coupling between the S and TT states, while ω_i and g_i stand for the frequency and coupling constant of the vibrational mode q_i . The term $H_i = -(\vec{d}\vec{E})$ elucidates the coupling of the G to S electronic excitation with the applied electromagnetic field within the dipole approximation.

1.2. Vibronic model for calculating coherent SF yield

The vibronic model represented by equations (C. 4)-(C. 8) was solved numerically with the method described in ref [133]. The vibronic eigenfunctions are expressed as follows:

$$\psi_{\alpha} = \chi_{\alpha}^{(G)}(q)\psi^{(G)} + \chi_{\alpha}^{(S)}(q)\psi^{(S)} + \chi_{\alpha}^{(TT)}(q)\psi^{(TT)} \quad (C. 9)$$

, where $\psi^{(G)}$, $\psi^{(S)}$ and $\psi^{(TT)}$ are electronic parts of the G, S and TT states wavefunctions; $\chi_{\alpha}^{(G)}$, $\chi_{\alpha}^{(S)}$ and $\chi_{\alpha}^{(TT)}$ are vibronic parts.

When exclusively considering transitions from the ground vibronic state, the absorption spectrum is proportional to $P_{0\alpha}^{(S)} = \left| \chi_0^{(G)}(q) \chi_{\alpha}^{(G)}(q) \right|^2$, contribution of the TT state to vibronic state $\alpha\alpha$ is characterized by $P_{\alpha}^{(TT)} = \left| \chi_{\alpha}^{(TT)}(q) \chi_{\alpha}^{(TT)}(q) \right|^2$. Therefore, the probability of generating TT state with photoexcitation can be calculated as the product $P_{0\alpha}^{(S)} \times P_{\alpha}^{(TT)}$.

In vibronic model, two effective mode approach has been used: one high frequency mode $\omega_1 = 1370 \text{ cm}^{-1}$ and one low frequency mode $\omega_2 = 200 \text{ cm}^{-1}$. The $H_{vib}^{(S)}$ parameters (C. 6) were chosen in a way that the experimental absorption spectrum (in solution) is well reproduced, while the

$H_{vib}^{(TT)}$ parameters (C. 7), which takes into account the coupling to a low frequency mode, were chosen to reproduce the reorganization energy related to $S \rightarrow TT$ transition.

III. Oscillatory features in transient absorption

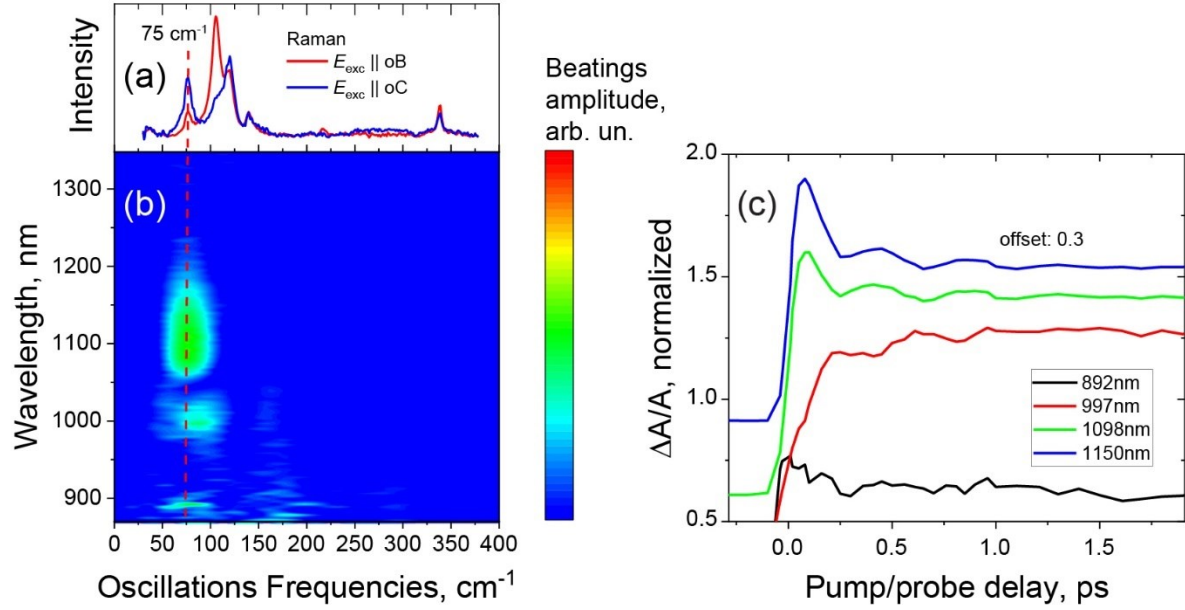


Fig. C3. Coherent oscillations in 2D TA map measured with 200-fs time resolution at room temperature. (a) Non-resonant Raman data used for the interpretation of the results. (b) the map of coherent beatings as a function of the probe energy. (c) The representative time-domain traces at different probe wavelengths.

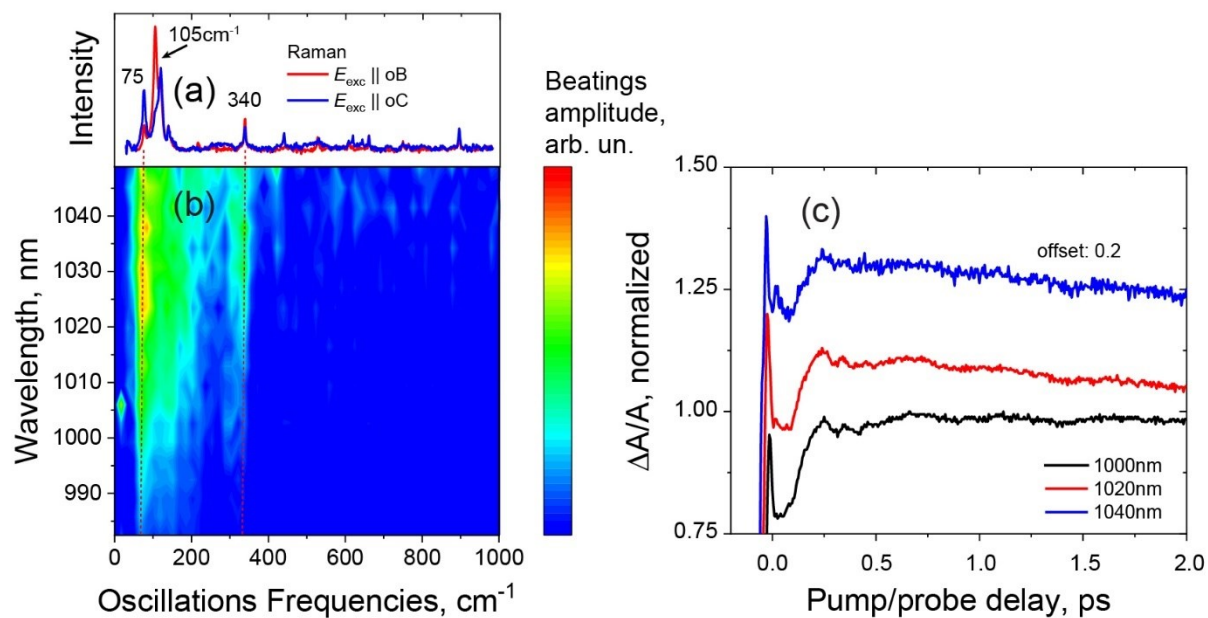


Fig. C4. Coherent oscillations in 2D TA map measured with 10-fs time resolution at room temperature. (a) Non-resonant Raman data used for the interpretation of the results. (b) the map of coherent beatings as a function of the probe energy. (c) The representative time-domain traces at different probe wavelengths.

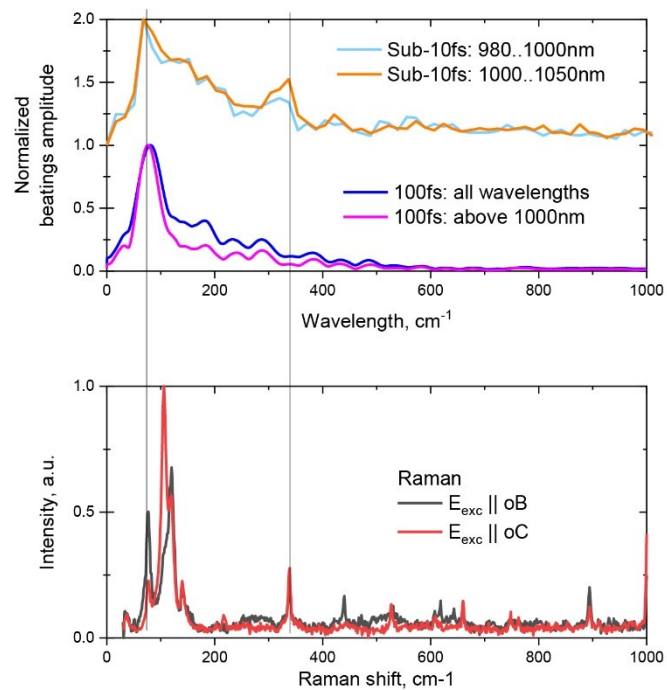


Fig. C5. Analysis of coherent oscillations in TA measured with 10-fs and 200-fs time resolution at room temperature. (top) the coherent beating spectra at different probe wavelengths. (bottom) Non-resonant Raman data used for the interpretation of the results.

Appendix D. Supporting information for Part 4

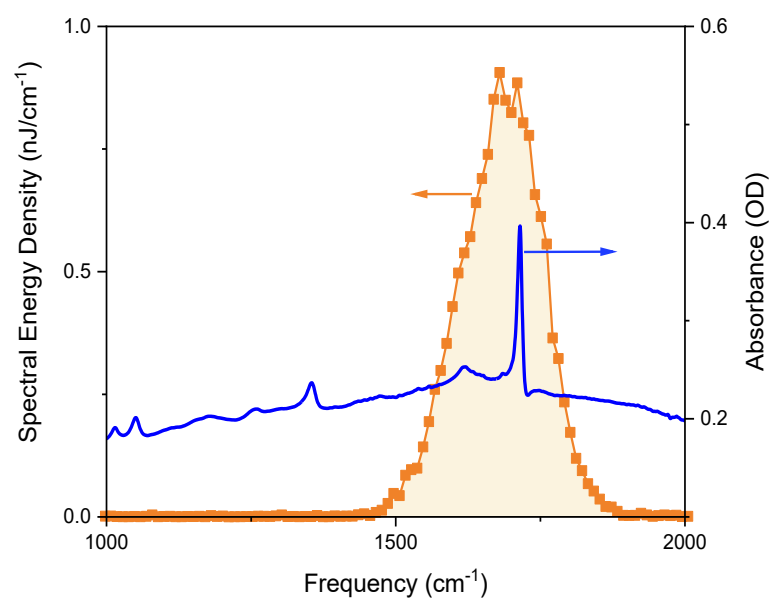


Fig. D1. IR spectra of an FAPbBr₃ device (blue curve), overlaid on the spectrum of the IR pre-excitation pulse used in PC VIPER experiments (orange curve).

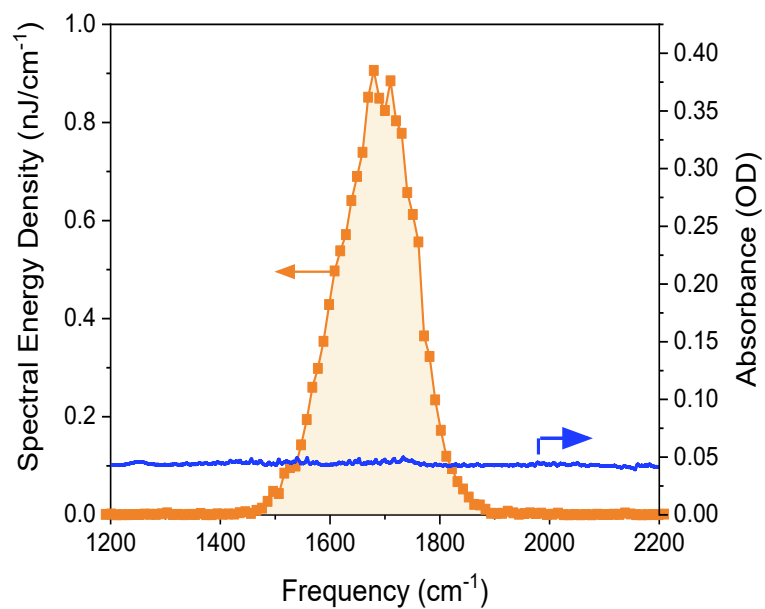


Fig. D2. IR spectra of a CsPbBr_3 device (blue curve), overlaid on the spectrum of the IR pre-excitation pulse used in PC VIPER experiments (orange curve).

Appendix E. Supporting information for Part 5

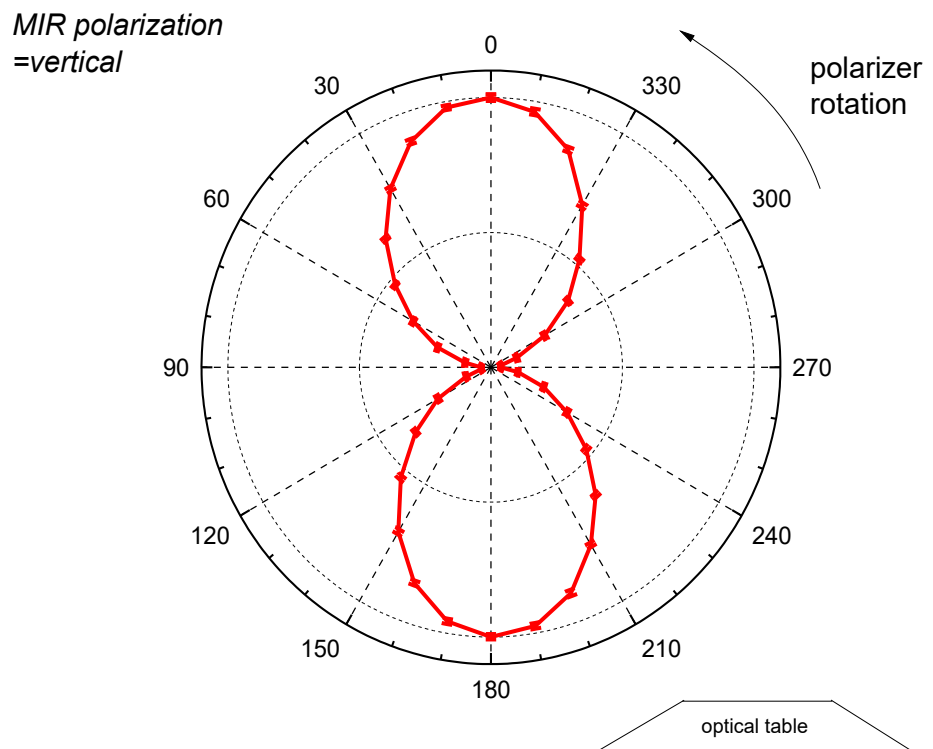


Fig. E1. MIR intensity dependence on a polarizer rotation. 0 and 180 points corresponds to the vertically oriented polarizer axis relatively to the optical table. The maximum intensity at this position of the polarizer as well as the shape of the curve indicates that the MIR beam is linearly polarized with polarization perpendicular to the pane of the optical table.

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