Impact of Structural Modifications on Ultrafast Correlation-Driven Charge Migration in Organic Molecules: For Molecular Engineering

PhD Thesis Booklet

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Introduction

In the natural world we can witness many different photo-chemical or photo-catalytic reactions governing photosynthesis, radiation damage, gene mutation and many other biological processes. The understanding and artificial replication of these processes can help humankind in the development of new chemical synthesis techniques and in the generation of clear energy. All these processes are mainly dependent on the quantum chemical dynamics of electrons and nuclei. This dependence is due to the overlaps between the atomic orbitals, which determine the formation of molecular bonds that control the mobility of charge and hence the chemical reactions. Therefore, investigation of the relation between the migration of charge and the rearrangement of nuclei is of fundamental interest. Energy absorption by a molecule during such photo-induced processes results in physical and chemical changes; to foresee them it is also essential to thoroughly understand the molecular properties in the ground, excited and ionic states. In addition to photons, molecular orbitals excitation can be further influenced by the different external factors such as solvent, temperature, or intermolecular interactions. Depending on these influences, the excitation process can lead to different chemical reactions, charge transfer, fluorescence, or fragmentation dynamics. Understanding the molecular response under different conditions will also foster efficient molecular designing, which will boost the integration of organic molecules in optoelectronic devices, organic or hybrid solar cells; in drug delivery, tumour cell detection; to name a few. The biggest question researchers now face is how to trigger, trace and control these responses? It is also important to note the timescales involved in studying each of these processes, which can vary from the attosecond (as, 10^{-18} s) to the femtosecond (fs, 10^{-15}s) domains.

The timescale involved in the various responses is important as, initially, within a few fs, before the onset of nuclear motion, one can observe only pure charge migration dynamics. Due to their light mass, electrons move faster in comparison to nuclei. Hence, from the as to the sub-fs timescales one can safely ignore the motion of the nuclei. Beyond the sub-fs timescale, the motion of the electrons starts to couple with the nuclei and this coupled electron-nuclear dynamics eventually leads to the rearrangement of nuclear positions within the molecule. To study the above mentioned motions, one needs to understand various electronic structures, vibrational modes, and electron-nuclei coupled interactions for a given system. Additionally, to measure these motions one needs extremely advanced, higher resolution techniques capable of capturing such ultrafast dynamics. Note that tracing such ultrafast processes both theoretically and through experimental techniques is

not trivial.

Over the years, with the advancements in laser sources, it is possible to achieve temporal resolution as well as spatial resolution at the atomic scales. Lasers can be used not only to explore the fundamental properties of charge dynamics, but also to control them. Lasers can also be used for freezing an atomic or molecular system far from its equilibrium and for observing the real-time vibrational motion[1]. Using a laser pulse to steer a chemical reaction in the desired channel is today called "femtosecond chemistry", which has become a very well established field of research. The persistent efforts by researchers to understand and visualize the motion of charge in real time gave birth to something we today call "attosecond science". A new paradigm in the field of attosecond science or chemistry is to use charge dynamics and quantum interference to influence chemical reactions. The investigation of such dynamics experimentally is an extremely challenging task. Until now, several different schemes were employed to study charge migration dynamics for molecular systems both in gaseous and liquid phases[2]. These experiments demonstrated that charge migration dynamics can be captured and reconstructed indirectly by measuring the yield of fragments[3] for doubly positively charged molecular ions at different delays between XUV and IR pulses, or directly via high harmonic generation using intense ultrashort laser pulses [4, 5]. To access and control the electron motions at such an ultrafast timescale can possibly be central for the optimization of the charge transfer routes in a molecule in a pre-determined, tailored manner. Dedicated research efforts – resulting in sophisticated models which can then trace the charge dynamics based on the observation of fragmentation channels – were initially reported by R. Weinkauf et al.[3]. Incorporation of the aligned molecules to measure the high harmonic signal was reported by P. Kraus et. al. to reconstruct charge migration dynamics[6]. In this report they measured the high harmonic spectra for the same molecule with different angles between the aligned molecules and laser pulse polarization. Current state-of-the-art HHG-driven *as* setups for XUV-pump–XUV-probe experiments are yet to overcome certain bottlenecks for full implementation. There are a few facilities around the world, including ELI ALPS[7], and XFEL[8] that have the potential to host such experiments in the near future. Such experiments can help understand the correlated charge migration dynamics and electron-nuclei coupled non-adiabatic charge dynamics in real time.

Theoretical developments have played an important role in the advancement of attosecond and femtosecond science. With theoretical advancements in density functional theory (DFT) and time-dependent density functional theory (TDDFT), it is now possible to study the intramolecular or intermolecular charge transfer

for larger systems (>100 atoms) in the static regime[9]. Further developments are in progress to study the charge transfer dynamics by investigating the crossing between the potential energy curves[10]. Such methods were very useful, and showed promising results. A huge advantage of using the DFT method is the possibility to handle larger systems in a realistic environment. This is particularly important when the basic electronic, or vibrational properties of the system are to be explored. For example, using DFT based calculations one can create databases for electronic and structural properties for a large number of molecules. These databases can be further evaluated to select effective systems for photo-induced charge transfer processes[11]. These databases can also be used for machine learning and for further molecular modelling[12]. However, it is important to note that the usual DFT approach, and the resulting databases are based on ground state electronic properties, and do not shed light on the temporal evolution of the electronic cloud during different chemical processes, and lack information on real-time charge migration dynamics.

The pioneering work by Cederbaum and Zobeley paved the way for studying real-time ultrafast charge migration[13]. Their results showed that the removal of charge from a molecular orbital can lead to the creation of an electron wavepacket. This electron wavepacket (in static nuclei approximation) is created by the excitation of several cationic states simultaneously. Furthermore, this wavepacket can be evolved in time. Using this method, several bio-relevant and astronomically important molecules were studied over the past few years. In a report by A. Marciniak et al., polycyclic aromatic hydrocarbons (PAHs) were studied using experimental and theoretical methods[14]. They measured ultrafast relaxation in a few tens of femtoseconds[14], and showed the transfer of energy from the electronic to vibrational degrees of freedom. This ultrafast charge migration method has also been used in the development of molecular modelling by V. Despre et. al., who studied the effect of carbon chain on the charge migration time[15].

In this thesis, I aim to understand and correlate the variation in charge migration dynamics with the change in molecular structure. For this study I investigated the dynamics in different timescales with appropriate quantum mechanical simulation methods. The analysis of these results is important for the development of molecular modelling. I examined how certain structural engineering of molecules can prominently impact charge reorganization over different parts of the molecular backbone, resulting in the ultrafast spatial rearrangement of electron density. I elucidated how charge transfer and charge migration critically depend on the factors such as the extent of π-conjugation, the strength of the electron correlation, arrangement of nuclei and the symmetry for the excited molecular orbitals.

My analysis revealed the differences in the ultrafast charge transfer, redistribution of the electronic cloud and charge migration processes in the context of chemical and structural variations in multi-nuclear systems. In this thesis I identify the exact time when the onset of the correlation effect in the attosecond timescale is observed. Furthermore, I present the calculations for prototype systems to study the ultrafast charge migration dynamics, which can be used by the experimental groups. To capture charge dynamics with experimental techniques, molecular alignment is an important factor to improve the signal to noise ratio. I included the quantum mechanical analysis to improve the alignment and orientation of polyatomic molecules – particularly for laboratory conditions and laser parameters as available in state-of-the-art laser facilities like ELI ALPS.

Methodology

I present a brief description and insights into different quantum mechanical approaches I used in the simulation of intramolecular charge transfer triggered by photo-excitation. I first calculated the photo-absorption spectra and the transition charge densities with the linear response TDDFT method. I then identified the excited states, where the charge transfers from the donor to the acceptor group in a large molecule. The calculated absorption spectra includes the solvent effect, which was applied with the conductor like polarizable continuum model (CPCM) [16]. I also used the semi-classical theory to evaluate the charge transfer rate equations. This theory was developed by Marcus [17], whereas the quantum mechanical treatment was given by Jorther et al. [18]. Assuming a maximum transfer rate, Gibbs free energy is taken approximately equal to the reorganization energy ($\lambda = \lambda_e + \lambda_h$), where $\lambda_i = (E_0^{\pm} - E_{\pm}) + (E_{\pm}^0 - E_0)$. Energies of the neutral and the ionic (cation or anion) species are given by E_0 and $E_{\pm}$, respectively, whereas the energies of the ionic and the neutral species with geometries of the neutral and ionic species are $E_{\pm}^0$ and $E_0^{\pm}$, respectively. To study the intramolecular charge transfer I analyzed changes in the structural parameters of the molecule in its excited state with respect to the molecule in its ground state. The large structural variations show which groups in the large molecule actively participated in the charge transfer, which is done by indirectly correlating and assuming that the structural changes are due to the charge transfer. A similar analysis was performed by comparing the change in the structural parameters of a molecule in the cationic state with respect to the ground state. Investigating the changes in the cationic state is important as in a solar cell the organic molecule remains in this state for a few picoseconds before it undergoes regeneration. Using this method I presented

the results from our publication [T1] and summarized here as Thesis point 1 and as Chapter 3 in the main thesis.

Then for small systems I investigated the photo-ionization induced charge migration dynamics with the non-Dyson algebraic diagrammatic construction with the third order permutation, also known as ADC(3) method. In the non-Dyson ADC(3) method the electron affinity and ionization part of the propagator are decoupled and each part is allowed to propagate independently. In this approach the Green's function has the following non-diagonal representation

$$G(\omega) = f^\dagger(\omega - L - D)^{-1}f \quad . \tag{1}$$

The latter is obtained through the representation of the Green's function in the complete set of so-called intermediate states, $|\tilde{\Psi}_n^{N-1}\rangle$, where 'n' in the subscript runs over the excitation classes: 1h, 2h1p; 3h2p and the ionization energy ω. In the Intermediate States Representations (ISR) the secular matrix is then given by

$$(L + D)_{ij} = \langle\tilde{\Psi}_I^{N-1}|E_0^N - H|\tilde{\Psi}_n^{N-1}\rangle \quad . \tag{2}$$

The effective transition moments "f_{1q}" is given by

$$f_{1q} = \langle\tilde{\Psi}_I^{N-1}|\hat{a}_q|\Psi_0^N\rangle \quad . \tag{3}$$

The ISR and the effective transition moments are constructed in the ADC procedure through the perturbation theory of the ground-state Ψ_0^N.

To trace the charge transfer within the molecule and associated electron dynamics, it is convenient to construct and analyze the time-dependent hole density $Q(\overrightarrow{r}, t)$ created by sudden ionization, and then solely driven by electron correlation [13]. $Q(\overrightarrow{r}, t)$ describes the hole density at position r and time t, and during the construction it is normalized at every time step (see Eq.4). The second-quantization representation of the density operator within a one-particle basis is given by

$$Q(\overrightarrow{r}, t) = \langle\Psi_0|\hat{\rho}(\overrightarrow{r}, t)|\Psi_0\rangle - \langle\Phi_i|\hat{\rho}(\overrightarrow{r}, t)|\Phi_i\rangle \tag{4}$$

$$= \rho_0(\overrightarrow{r}) - \rho_i(\overrightarrow{r}, t) \quad ,$$

where operator $\hat{a}_p^\dagger$ creates an electron in orbital ϕ_p and $\hat{a}_p$ destroys an electron to create a hole in orbital ϕ_p. Within this representation, hole density takes the form

$$Q(\overrightarrow{r}, t) = \sum_{p,q} \phi_p^*(\overrightarrow{r})\phi_q(\overrightarrow{r})N_{pq}(t) \quad , \tag{5}$$

where $N_{pq}(t)$ represents the hole density matrix. The hole density is given as a difference between the electronic density of neutral and single positively charged cation in Eq.4. Here $\hat{\rho}$ is the density operator, $|\Psi_0\rangle$ is the ground state of the neutral, and $|\Phi_i\rangle$ is the initially prepared cationic state. $\rho_i(\vec{r}, t)$ in Eq.4 is a time-dependent density operator. The ultrashort laser field has a broad bandwidth and this can excite more than one electronic state. To address this problem we used an incoherent sum of the correlated charge density at each time step. This includes the effect from all the excited molecular orbitals by a broadband laser pulse. Using this method I presented the results from our publication [T2 and T3] and summarized them here as Thesis points 2 and 3, respectively, and as Chapters 4 and 5 in the main thesis. Furthermore, I constructed the vibronic coupling Hamiltonian to study the electron-nuclei coupled non-adiabatic dynamics. The results for this are presented as Chapter 6 in the main thesis.

To study the laser-induced alignment of molecules I solved the time-dependent Schrödinger equation (TDSE) given below, using the LIMAO code[19]

$$i\hbar\partial_t|\Phi(t)\rangle = \hat{H}(t)|\Phi(t)\rangle = (\hat{H}_0 + \hat{H}_{\text{ext}}(t))|\Phi(t)\rangle \tag{6}$$

In the above equation the $\hat{H}_0$ part is the molecular field-free Hamiltonian. This Hamiltonian is constructed under the rigid rotor approximation, where no ro-vibrational coupling terms are considered. The laser-matter interactions are considered via the $\hat{H}_{\text{ext}}(t)$ term in Eq.6, this is the time-dependent part of the Hamiltonian. Depending on the pulse duration of the laser pulse, one can include or exclude the dipole moment interaction. For example, a short optical pulse oscillates faster compared to the rotational period of the molecule, as a result of which the dipole interaction can be neglected using the cycle-averaging method[20]. After solving the appropriate TDSE, we calculate the time-dependent degree of alignment for a symmetric top molecule using

$$\langle\cos^2(\theta)\rangle\,(t) = \langle\Phi(t)|\cos^2(\theta)|\Phi(t)\rangle \quad . \tag{7}$$

The angle between the lab-fixed z-axis and the molecular symmetry axis is given by θ. Using this method I presented the results as Thesis point 4 and as Chapter 7 in main thesis. The results are published as article [T4].

Summary

Recently organic structures have started to be used in several highly efficient and flexible opto-electronic solar cell and sensors devices, and they have also found application in tumour detection and radiation therapy. The organic compounds mainly play a role in charge and energy transfer in these devices. These molecules are typically large extended systems with a push-pull structure, where the photo-induced charge is transferred from the donor group to the acceptor group. For the efficient modelling of these large molecules it is crucial to understand charge dynamics in small groups used in molecular design. This understanding will aid in selecting, or modifying the groups, and in finding efficient ways to assemble different groups for effective charge transfer. In this thesis I have tried to answer the following questions to help molecular modelling: How can linear response calculations be used to study the charge transfer process in large molecules? Does the correlation effect play an important role in charge migration dynamics (CMD)? How long does a molecule take to respond to the triggered dynamics and can this be tuned by the tautomerism or isomerization of molecules? Does the incoherent CMD mask the dynamics in different tautomers? How long is it before the non-adiabatic dynamic processes start and can they vary with the vibrational degrees of freedom involved in electron-nuclei coupling? What are the important things to consider before measuring these dynamics experimentally? I summarize below the key points of this thesis answering the above questions.

Thesis point 1

Typically, in a large extended molecule the charge transfer process occurs through the π-conjugated structure. When designing these molecules, it is important to make sure that the charge is indeed transferred from the donor to the acceptor group and is not trapped by a π-spacer. It can be computationally and experimentally expensive to determine such a charge transfer. Hence, I proposed a novel way to analyze the charge transfer efficiency using static linear response method. I interpreted the charge transfer in the molecule by studying the modification in a molecular structure after photo-excitation and ionization to the cationic state, with respect to its ground state. This method is useful to perform cost-effective calculations for analyzing the molecules before their experimental synthesis. The use of structural modifications has been reported in literature to interpret the charge transfer in molecules, however only in one of the above mentioned states. I studied the modified structure for a molecule in both states. This approach was reported

for the first time (to the best of our knowledge) in the paper we published in [T1].

Thesis point 2

As mentioned earlier, the above method facilitates our understanding of the push-pull systems already used for photovoltaic or optoelectronic applications. However, studying the charge migration dynamics in the building blocks will help extensively in designing molecules. In Chapter 4 I studied the charge migration dynamics triggered by the sudden ionization of molecules like uracil. The response of the different molecular orbitals to such ionization is evaluated and investigated with the correlation effect. For a molecule with C_s symmetry, I found that the symmetric orbitals have similar response times, while the asymmetric molecular orbitals take longer to respond to sudden ionization. The response time of the asymmetric orbitals increases with the strength of the correlation effect. The response times by different orbitals in keto-uracil can be reduced by conversion to the enol-form via tautomerization. In enol-uracil the reduced response time is related to the greater delocalization of charge over the entire system in comparison to the keto-uracil molecule. The results for the *as* response were reported in [T2].

Thesis point 3

The visualization of charge migration dynamics will help massively not only in molecular modelling, but also in understanding the radiation damage in biological systems. When studying such dynamics experimentally, an ultrashort attosecond pulse is used, which can ionize a broadband of cationic states. I studied the femtosecond charge migration dynamics in the keto and enol forms of uracil after ionizing the outer valence orbitals separately and incoherently considering the broadband of an ultrashort pulse. During this investigation, we observed strong correlation effects in the asymmetric orbitals. The charge density is more delocalized in the symmetric orbitals. The difference in charge migration between the keto-enol tautomers and the two types of orbitals of uracil remains even after incoherent ionization. The results for the *fs* charge migration dynamics were reported in [T3].

Thesis point 4

The study of charge migration dynamics using advanced experimental methods requires highly aligned molecules. To study and control the alignment of the molecules under a laser field we need to understand the role of the rotational states in laser-induced molecular alignment and orientation dynamics. In Chapter 7, using a prototype system, CH_3F, I studied the population variation of the rotational states by tuning experimentally feasible laser pulse parameters. In this work I observed two different types of alignment behaviours which were termed as conventional and unconventional revivals. These two types of behaviour are correlated with the nature of the rotational states excited by the selected laser parameters. Hence, I reported the importance and ways to tune the rotational states to enhance the laser-induced alignment of the molecules in our published article [T4][21].

The main emphasis of this doctoral thesis is to gain atomistic level understanding of the photo-induced charge migration and charge transfer processes in extended molecular systems. Such ultrafast responses govern the photophysical and photochemical processes of the molecules and solid-state materials. Hence, the overall results of this thesis can be used by chemists in molecular designing, and by biologists in understanding the effect of radiation therapy on the nucleobases. Several interesting works have already been published in related topics, however there still remain a few gaps that need to be addressed. Using suitable and optimized computation and analysis methods presented in this thesis, it is possible to explain charge hopping, isomerization or fragmentation of nucleobases in DNA by comparing pre- and post-ionization conditions, or why and how the efficiency of the dye molecules vary upon shuffling the position of the π-spacer group[22]. I explain how the microscopic features obtained by the atomic-level simulations can be correlated to the macroscopic level responses of the molecules captured experimentally. The calculation of the exact time and direction of charge migration as presented in this thesis can be used to tailor and design extended molecules with improved and desired features. One can further utilize this study for evaluating the molecules to increase the interfacial charge dynamics, stability, efficiency and lifetime of perovskite materials[23, 24, 25]. This study can be extended to understand the influence of solvent or intermolecular interactions[26, 27] on the charge migration dynamics and the nonlinear optical properties such as high harmonic spectra[28]. Hence, we hope our results will encourage and inspire further research in the direction of molecular modelling.

Magyar nyelvű összefoglaló

Az utóbbi időkben szerves molekulák felhasználásával nagy hatásfokú és flexibilis optoelektronikai napelem cellák és szenzorok váltak elérhetővé. Ilyen molekulák a tumordetektáláshoz és sugárkezeléshez használt eszközökben is alkalmazhatók, ahol leginkább a töltés- és energiaátadásban játszanak szerepet. E molekulák általában nagyméretű, push-pull szerkezettel rendelkező rendszerek, ahol a foton által előidézett töltés a donor csoportról az akceptor (fogadó) csoportra adódik át. Hatékony modellezésük érdekében elengedhetetlen a töltésdinamika megértése a molekulák tervezése során használt kisebb csoportoknál. E tulajdonságok ismerete segít a csoportok kiválasztásában, módosításában, és a legjobb töltésátadást biztosító csoportok hatékony kialakításában. Disszertációmban igyekszem választ adni a molekulamodellezésnél felmerülő számos kérdésre: Hogyan lehet statikus számításokkal tanulmányozni a töltésátadási folyamatot nagy molekulákban? Fontos szerepet játszik-e a töltésmigrációs dinamikában (CMD) a korrelációs effektus? Mennyi időt vesz igénybe a molekula válasza egy kiváltó folyamatra és lehet-e ezt tautomériával vagy izomériával hangolni? Elfedi-e ez az inkoherens CMD a különböző tautomerek dinamikáját? Mennyi időbe telik a nem-adiabatikus dinamikai folyamat elindulása, és befolyásolható-e ez az idő az elektron-atommag csatolásban részt vevő rezgési szabadsági fokokkal? E dinamikai folyamatok kísérleti mérése előtt mely fontos paramétereket szükséges figyelembe venni? A kérdések megválaszolásához doktori munkámat az alábbi tézispontokban foglaltam össze:

1. tézispont

A kiterjedt nagy molekulákban a töltésátadási folyamat általában a π-konjugált struktúrán keresztül játszódik le. Ilyen molekulák tervezése esetén fontos megbizonyosodni arról, hogy a töltés valóban a donortól az akceptor csoportba adódik át, és nem csapdázódik egy π-távolságtartó (spacer) csoportban. E töltésátadási folyamat megállapítása mind kísérleti, mind szimulációs úton rendkívül erőforrásigényes feladat.A molekulán belüli töltésátadás értelmezéséhez foton által gerjesztett és kationos állapotba helyezett molekulaszerkezet változását tanulmányoztam az alapállapothoz viszonyítva. E módszer alkalmas a kevésbé erőforrásigényes számítások elvégzésére, így a molekulák kísérleti szintetizálás előtti elemzéséhez. A molekulákban történő töltésátadás értelmezése céljából előidézett, molekulaszintű strukturális változásokról már több cikk is megjelent, de a korábbi közlemények csak az egyik fent említett állapotra koncentráltak. Dolgozatomban mindkét állapotban tanulmányoztam a molekulaszerkezetet. Ez a megközelítés (legjobb tu-

domásunk szerint) először került közlésre cikkünkben[T1] és e dolgozat 3. fejezetében.

2. tézispont

Ahogyan már korábban említettem, a fenti módszer megkönnyíti a fotovoltaikus és optoelektronikus területeken már alkalmazott push-pull rendszerek megértését, ám a rendszertervezés során különösen fontos a részegységek töltésmigrációs dinamikájának tanulmányozása. A 4. fejezetben az azonnali ionizáció által kiváltott töltésmigrációs dinamikát vizsgáltam molekulákban, például uracilban. Az ilyen ionizációs folyamatra a különböző molekulapályák által adott válasz elemzése és vizsgálata korrelációs effektus segítségével történik. A C_s szimmetriával rendelkező molekulákra azt állapítottam meg, hogy a szimmetrikus molekulapályák hasonló válaszidővel rendelkeznek, de az aszimmetrikus pályák esetén az azonnali ionizációra adott válasz hosszabb időt vesz igénybe. Az aszimmetrikus pályák esetén a válaszidő a korrelációs effektus erősségével nő. A válaszidők csökkenthetők a keto-uracil molekula enol-uracil molekulává való módosításával tautomerizációs folyamaton keresztül. Enol-uracil esetén a válaszidő rövidebb, hiszen a töltés nagyobb delokalizációval rendelkezik az ionizációt követően. Az eredmények erre az attoszekundumos időtartamú válasszal kapcsolatos eredmények a [T2]-ben kerültek közlésre.

3. tézispont

A töltésmigráció dinamikájának vizualizációja nemcsak a molekulatervezést, hanem biológiai rendszerek sugárzási károsodásainak megértését is segíti. Ezen effektusok kísérleti úton való megfigyelése a szükséges időbeli felbontás miatt csak ultrarövid, attoszekundumos hosszúságú fényimpulzusok alkalmazásával lehetséges, amelyek kationikus állapotok széles tartományát képes ionizálni. Femtoszekundumos töltésmigrációs dinamikát vizsgáltam az uracil keto és enol változatában azután, hogy a külső vezetési elektronpályákról egyesével és inkoherens módon ionizáció történt szélessávú, ultrarövid pulzussal. A vizsgálat során azt találtuk, hogy a töltés erős korrelációs hatást gyakorol az aszimmetrikus molekulapályákra. A töltéssűrűség jobban delokalizált a szimmetrikus pályákon. A töltésmigráció különbsége a keto-enol tautomerek és az uracil két különböző molekulapályája között még inkoherens ionizáció után is fennáll. A *fs*-os töltésmigrációs dinamikával kapcsolatos eredményeket a [T3]-ben publikáltuk.

4. tézispont

A töltésmigráció összetett kísérleti módszerekkel való tanulmányozásához elengedhetetlen a molekulák irányítottságának nagyfokú beállítása. molekula lézertér általi irányítottságának tanulmányozása és szabályozása érdekében nélkülözhetetlen a folyamat és a molekuláris forgási állapotok közötti összefüggés megértése. A 7. fejezetben prototípus rendszeren (CH$_3$F) tanulmányoztam a forgási állapotok populációjának változását a lézer paramétereinek kísérleti változtatása nyomán. Kétféle molekulabeállítási viselkedést, úgy nevezett konvencionális és nemkonvencionális revivalt figyeltem meg. E két viselkedés összefüggésben áll a kiválasztott lézerparaméterekkel történő gerjesztés nyomán kialakuló forgási állapotokkal. Tudományos publikációban [T4] ismertettük a forgási állapotok finomhangolásának szükségességét a lézertér által előidézett molekula-irányítottság javítása érdekében.

Doktori értekezésem fő célja a nagy molekulákban foton által kiváltott töltésmigrációs és töltésátadásos folyamatok atomi szintű megértése. Ezek az ultragyors válaszidők befolyásolják a molekulákban és szilárd anyagokban lejátszódó fotofizikai és fotokémiai folyamatokat. Így a jelen dolgozatban bemutatott eredmények főként a molekulatervezéssel foglalkozó vegyészeknek lehetnek hasznosak, valamint segíthetnek a biológusoknak megérteni, hogyan hat a sugárterápia a nukleobázisokra. A témában már több érdekes folyóiratcikk is megjelent, de még vannak tisztázandó kérdések. A disszertációban bemutatott optimalizált szimulációs módszerek és elemzések felhasználásával megérthetjük a töltésugrást, az izomerizációt vagy a nukleobázisok fragmentációját a DNS-ben az ionizáció előtti és utáni állapotok összehasonlításával, valamint azt, hogy miért és hogyan változik a festékmolekulák fontonkonverziós hatásfoka a π-távolságtartó (spacer) csoport áthelyezése miatt. Ismertetem, hogy az atomi szintű szimulációval kapott mikroszkopikus tulajdonságok milyen összefüggésben állnak a makroszkopikus szintű, kísérletileg is mérhető molekuláris válaszokkal. Ahogy a dolgozatban kifejtem, a töltésmigráció pontos idő- és iránybeli függésének kiszámítása felhasználható arra, hogy a molekulatervezés során fokozottan előtérbe kerüljenek a nagy molekulák kívánatos tulajdonságai. A tanulmány segítségével értékelhetők a molekulák annak érdekében, hogy növeljük a perovszkit anyagok határfelületi töltésdimanikáját, stabilitását, hatásfokát és élettartamát. [23, 24, 25] A dolgozat tovább bővíthető, hogy megértsük a különböző közegek vagy molekulák közötti kölcsönhatások hatását a töltésmigrációs dinamikára[26, 27] és olyan nemlineáris

optikai tulajdonságokra, mint magasharmonikus-keltés spektruma.[28] Reméljük, hogy az eredményeink további kutatásokra ösztönöznek és újabb utakat nyitnak a molekulamodellezés irányában.

Publications

Journal publications

IF: Impact factor

[T1] **Kalyani Chordiya**, Ehesan Ali, Mousumi Upadhyay Kahaly Photoexcited Intramolecular Charge Transfer in Dye Sensitizers: Predictive In Silico Screening for Dye-Sensitized Solar Cell Devices. *ACS Omega*, **7**, 13465-13474, 2022. (IF: 4.132)

[T2] **Kalyani Chordiya**, Victor Despré, Mousumi Upadhyay Kahaly, and Alexander I. Kuleff Distinctive onset of electron correlation in molecular tautomers. *Physical Review A*, **105**, 062808, 2022 (IF: 2.971).

[T3] **Kalyani Chordiya**, Victor Despré, Balázs Nagyillés, Felix Zeller, Zsolt Divéki, Alexander I. Kuleff, and Mousumi Upadhyay Kahaly Photo-ionization Initiated Differential Ultrafast Charge Migration: Impact of Molecular Symmetries and Tautomeric Forms. *Physical Chemistry Chemical Physics, in press*, 2022 (IF: 3.945).

[T4] **Kalyani Chordiya**, Irén Simkó, Tamás Szidarovszky, Mousumi Upadhyay Kahaly Achieving high molecular alignment and orientation for CH3F through manipulation of rotational states with varying optical and THz laser pulse parameters. *Scientific Reports*, **12**, 1-10, 2022 (IF: 4.996).

Further related publications

[O1] Yanyan Duan, **Kalyani Chordiya**, Mousumi Upadhyay Kahaly, Freddy E Oropeza, Víctor A de la Peña O'Shea, De-Yi Wang, Ruben D Costa Rational Amphiphilic Ligand Engineering Enables Enhanced Stability and Efficiency of CsPbBr3 Nanocrystals Based Light Emitting Diodes. *Advanced Optical Materials*, 2201176, 2022 (IF: 10.05).

[O2] He Zhao, **Kalyani Chordiya**, Petri Leukkunen, Alexey Popov, Mousumi Upadhyay Kahaly, Krisztian Kordas, Satu Ojala Dimethylammonium iodide stabilized bismuth halide perovskite photocatalyst for hydrogen evolution. *Nano Research*, **14**, 1116-1125, 2020 (IF: 9.240).

[O3] **Kalyani Chordiya**, Gergely Norbert Nagy, Mousumi Upadhyay Kahaly Synthesis Techniques for Low Dimensional Magnets. *CRC Press, Fundamentals of Low Dimensional Magnets*, Chapter 4, 2022.

[O4] Irén Simkó, **Kalyani Chordiya** Attila Csaszar, G, Mousumi Kahaly, Upadhyay, Tamás Szidarovszky A quantum-chemical perspective on the laser-induced alignment and orientation dynamics of the CH3X (X = F, Cl, Br, I) molecules. *Journal of Computational Chemistry*, **43**, 519-538, 2022 (IF: 3.672).

[O5] Swathi Erekath, **Kalyani Chordiya**, K V Vidhya, Mousumi Upadhyay Kahaly and Sreeram K Kalpathy Self-aggregation, H-bonding, and Photoresponse in Film and Solution States of Azobenzene Containing Polyurea. *Physical Chemistry Chemical Physics*, **24**, 23447 - 23459, 2022 (IF: 3.945).
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Declaration of Co-authorship

I, Mousumi Upadhyay Kahaly hereby declare that as a co-Authors I recognize the thesis points 1 to 4 for Ref. [1-4] given below as individual result by Kalyani Chordiya and declare that I will and did not use these results to obtain any scientific degree.

1) Photoexcited Intramolecular Charge Transfer in Dye Sensitizers: Predictive In Silico Screening for Dye-Sensitized Solar Cell Devices, K. Chordiya, E. Ali, M. U. Kahaly, ACS Omega, 7 (2022), 13465-13474.

2) Distinctive onset of electron correlation in molecular tautomers, K. Chordiya, Victor Despré, M. U. Kahaly, and A. I. Kuleff, Physical Review A, 105 (2022), 062808.

3) Photo-ionization Initiated Differential Ultrafast Charge Migration: Impact of Molecular Symmetries and Tautomeric Forms, K. Chordiya, V. Despré, B. Nagyillés, F. Zeller, Y. Divéki, A. I. Kuleff, and M. U. Kahaly, Phys. Chem. Chem. Phys. (2022), just accepted.

4) Manipulation of Rotational States With Varying Pulse Parameter: Achieving High Molecular Alignment and Orientation for CH_3F, K. Chordiya, I. Simkó T. Szidarovszky, M. U. Kahaly, Scientific Reports 12.1 (2022): 1-10.

Date: *2022. 10. 04*

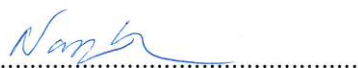...
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Date: *2022. 10.04, Szeged*
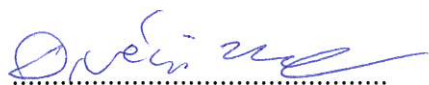
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Place and date: Budapest, 2022.10.4.

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