

2015-2016 Progress Report for DE-SC0012628: UCLA and ULg

During the second period, the UCLA-ULg group has pursued quantum dynamical simulations of electronic and nuclear motion triggered by a strong, short optical pulse towards steering chemical reactivity. We have also started the investigation of larger systems. In collaboration with the Li group, we have simulated the electronic dynamics of double ionization in the PENNA cation. The UCLA-ULg and the Schlegel groups jointly work on integrating methodologies for computing photoionization and strong field ionization widths.

1. Spectroscopic probing charge migration induced by ultrafast photoexcitation in N₂

The homonuclear N₂ molecule has no dipole when it is in a stationary state. Charge migration induced by an attosecond excitation can result in a time dependent dipole moment. Using the pulse parameters of the Li group to excite the N₂ molecule while retaining a full description of the nuclear motion we computed the resulting dipole moment of the molecule. Charge migration is faster than the nuclear motion so that there is a dipole only when the excited state is in the Franck Condon region of the ground state. Monitoring the dipole by inducing it to emit using a probe pulse can therefore serve as a sensitive test of charge migration. We have previously shown that the electronic dynamics in N₂ is strongly influenced by coupling of the diabatic valence and Rydberg states. If we remove this coupling, the dipole moment due to charge motion in the valence states clearly shows a recurrence as the wavepacket of the nuclear motion moves out of the Franck Condon region to the far away outer turning point, about 30 fs, and then back. Diabatic coupling to the Rydberg states brings population into the valence states and somewhat distorts this simple picture. These results have been published in the Journal of Physical Chemistry A.[1] We are currently computing the frequency spectrum that corresponds to probing the time changing dipole moment. The UC Berkeley group has measured this spectrum and they provided us with the parameters of their pump and probe pulses. The pump used is rather broad in energy and accesses ionizing states. To compare with these results we therefore need the transition dipoles to these states and we are currently computing them.

We are also reporting on the probing of charge migration in N₂ by Raman spectroscopy. This takes advantage of the large amplitude motion of the nuclear wavepacket on the diabatic potential of the valence state as noted above. Following its initiation, the nuclear wavepacket moves away from the Franck Condon region as determined by the ground state. When the wavepacket reaches higher internuclear distances it has transition dipoles to emit to high lying vibrational states on the ground electronic state. The wavepacket on the valence state reaches the outer turning point and is reflected and goes back to the Franck Condon region. It goes out again and so on. But the valence state potential is rather anharmonic so different vibrational energies have rather different vibrational frequencies and very quickly the nuclear wavepacket on the valence state bifurcates into many components. Figure 1 shows the absolute values of the amplitudes for emission from the nuclear wavepacket on the valence state to different vibrational states n of the ground electronic states as a function of time. The pump peak is at 12 fs. There are two columns for the two valence states of Σ and of Π symmetry. As indicated the results are

shown both without and with diabatic coupling to the Rydberg states. In the first period of the wavepacket motion it is seen how the motion on the valence state can emit to high n states. Then in the second round on the upper potential the nuclear wavepacket is seen to begin to bifurcate. When the diabatic coupling is on, top row, there are more components of the nuclear wavepacket motion because the somewhat higher lying Rydberg states feed into the valence state. The Rydberg states are about as tightly bound as the ground electronic state and so do not emit to higher n states. The Raman spectrum probes the valence state charge migration.

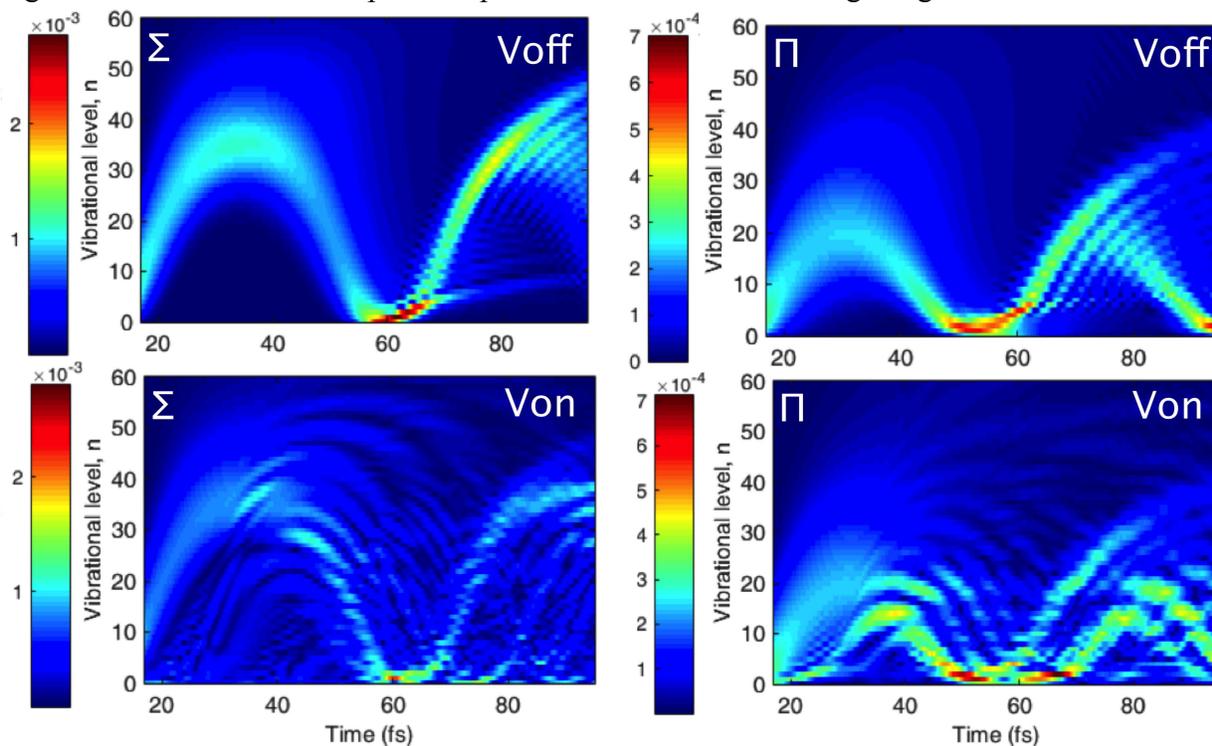


Figure 1. Emission probabilities, $|\langle b'(t)|n \rangle|$ (left column), and $|\langle b(t)|n \rangle|$ (right column), for the Σ and Π valence state respectively, computed with the diabatic coupling Voff (top) and Von (bottom). The carrier frequency of the ultrashort pulse is 13.61 eV and its width 1eV.

2. Control of fragmentation yields in the excited electronic states of LiH using the carrier envelope phase of a strong one cycle IR pulse.

We examined computationally how ultrashort polarized strong one cycle IR pulses can be used for steering coherent nuclear dynamics in LiH and controlling fragmentation yields.[2] The nuclear motion is described using the time-dependent Schrödinger equation on a grid on several coupled electronic states. The coupling to the strong field of the pump and probe pulses is included in the Hamiltonian as well as the non adiabatic coupling between the different electronic states. LiH possesses low lying Σ and Π states that can be selectively accessed by controlling the polarization of the pump pulse along the bond or perpendicularly to it. In addition, when using a one cycle pulse, controlling the carrier envelope phase (CEP) allows to select the states that will be coherently excited according to their polarity. Since the excited Σ states (except Σ_1) and all the Π states are repulsive, polarization and CEP control of the pump pulse leads to controlling the dissociation yields. In particular, our quantum dynamics

simulations show that the ratio of the fragmentation yields of the Σ_2 and Σ_3 states can be changed by a factor 10 when the CEP of a one cycle IR pulse polarized along the bond is switched from 0 to π , see figure 2. This control can be rationalized on the basis of the polarities of the Σ states. A simple qualitative summary is that successive excited states of Σ symmetry have opposite polarities. The GS is ionic in the sense of $\text{Li}^{\delta+}\text{H}^{\delta-}$. The first excited Σ_1 state has the charge transferred to the other end, $\text{Li}^{\delta-}\text{H}^{\delta+}$. The next excited, Σ_2 state is polar like the GS etc. These trends are seen not only in the dipole moments, but also in the transition dipole moments. In addition, Σ_1 , Σ_2 and Σ_3 dissociates to different Rydberg states of the Li atom, Li(2p), Li(3s) and Li(3p) respectively, which allows to measure the fragmentation yields of the different excited states.

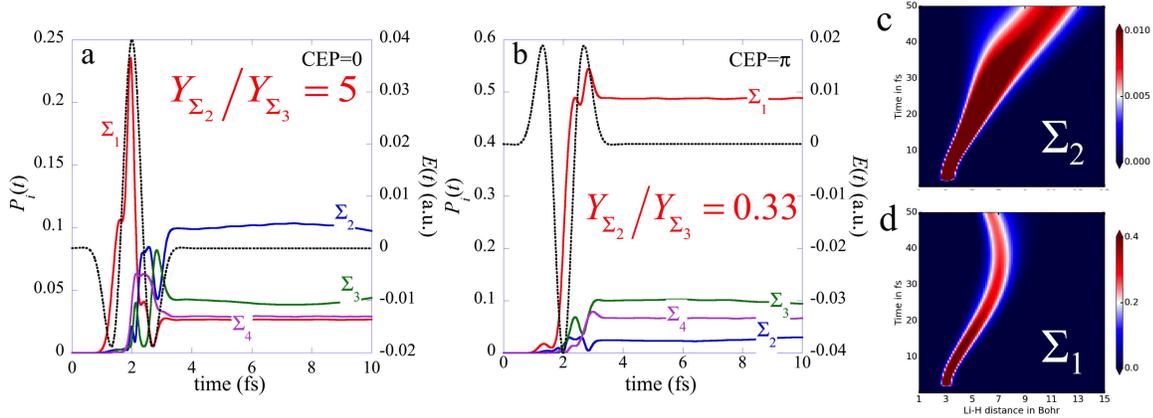


Figure 2. Control of the fragmentation of LiH by the CEP. Shown is the yield ratio $Y_{\Sigma_2}/Y_{\Sigma_3}$ using the CEP controlled one cycle 800nm pulse ($\sigma = 0.68$ fs, electric field strength=0.04 a.u. polarized along the molecular axis). Panels (a) and (b) show the computed populations in the Σ manifold below the IP for two pulses differing by the value of the CEP. The electric field time profile is shown in dots. Panels (c) and (d) show the wave packet dynamics for the CEP= π pulse for Σ_2 that dissociates and Σ_1 that does not.

In addition to probing the dynamics by following the fragmentation, we also report on probing the coherent vibronic wave packet using transient absorption spectra that results from the interaction of the molecular transition dipole with the electric fields of the pump and the probe pulses. The response, $S(\omega)$, retrieves the different time scales of the vibronic dynamics and probes the time evolution of the coherences.[2] It is defined [Gaarde, M. B. et al, Phys. Rev. A 83, 013419, (2011)] as $S(\omega) = -2\text{Im}[\mu(\omega)E^*(\omega)]$ where $\mu(\omega)$ and $E(\omega)$ are the Fourier Transform (FT) of the induced dipole $\mu(t)$ and of the electric fields, $E(t)$, of the pump and probe pulses respectively. Fig.3a shows the absolute value of the induced molecular dipole, $|\mu_z(\omega)|$, resulting from an excitation by the ‘-z’ pump pulse and probed by a one cycle UV 300nm ($|E_z|=0.005$, $\sigma=0.24$ fs) polarized along the molecular axis at a delay time, $\tau = 3$ fs. The frequency range is centered on the transition GS- Σ_1 , at 3.5 eV. Two time windows have been used for computing the FT of the molecular dipole. The shortest one, 80fs, can resolve the vibrational states of the GS (0.5 eV which corresponds to a period of 20 fs). The longer one of

160fs allows probing the much longer vibrational period of 80 fs (0.02 eV) of Σ_1 . Both the absorption and emission processes occurring during the pump and the probe pulses appear in the computed response function, $S(\omega)$, plotted in panels b and c for the short and the long time windows respectively. $S(\omega)$ is plotted as a heatmap of a delay time, τ , between the pump and the probe pulse (x axis) and the frequency of the response, ω (y axis). One clearly distinguishes along the y axis the transition frequency GS- Σ_1 at 3.5 eV, modulated by the 0.5 eV vibrational frequency of the GS in panel b. The vibrational period of Σ_1 is seen in panel c for which the FT is computed for a longer time window. In both panels b and c, the fast beating of the electronic coherence GS- Σ_1 (3.5 eV corresponds to 1.18 fs) appears along the delay time axis. We showed in ref [2] that the GS- Σ_1 electronic coherence survives hundreds of fs, modulated by the nuclear motion.

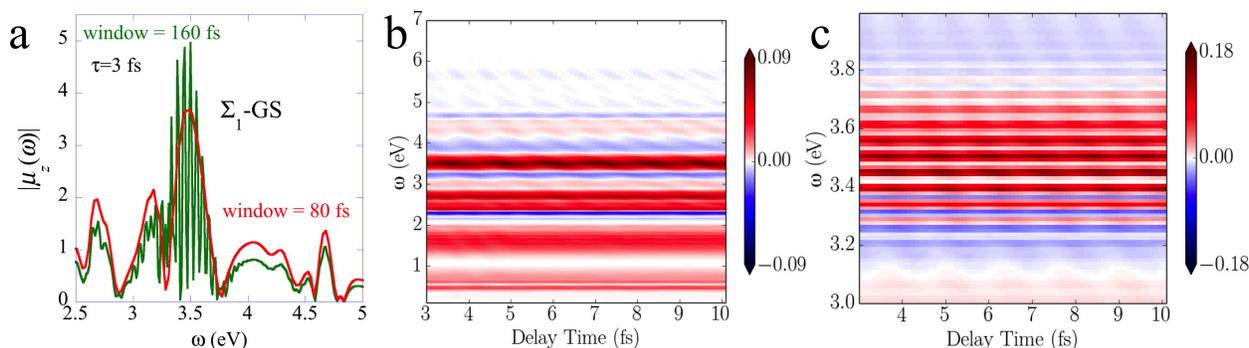


Figure 3. a) Absolute value of the FT of the molecular dipole, computed for two duration of the time window, 80 fs and 160fs as indicated. b) and c) Heatmaps of the response function computed for the 80fs and 160 fs time windows respectively. The 1fs beating of the GS- Σ_1 coherence are probed by the delay time between the pump and probe (x axis) while the vibrational frequencies on the GS and Σ_1 are clearly seen along the frequency axis y. Adapted from ref. [2].

3. Simulations probing the correlation in the double ionization in the modular PENNA molecule.

In the first project period the Li group reported a new experimental set-up able to measure the momentum electron correlation in double ionization. Results were presented for the non sequential double ionization in benzene. In close collaboration with the Li group, we investigated theoretically if this new experimental set-up could be used to probe charge migration in the cation of the modular PENNA molecule, $C_{10}H_{15}N$, a modular molecule where a phenyl is linking to a dimethyl amine by an ethylene bridge, see fig. 5a. We computed the electronic and photoionization dynamics of the PENNA molecule induced by a pulse similar to the ones used in the Li group, a 8.5 fs 800 nm IR pulse with a field strength of $2 \cdot 10^{12} \text{W/cm}^2$. The molecules are oriented along the direction of charge migration between the two moieties (x axis in the molecular frame). The pulse is circularly polarized in the (y,z) plane perpendicular to the direction of charge migration (x) so that the charge migration occurs field free. The electronic dynamics in the three manifolds of electronic states (neutral, cation and dication, see fig 5b) is computed for frozen nuclei. The pulse induces photoionization to the cation and the dication in a sequential way. The photoionization to the cation leads to a complex coherent superposition of electronic states of the cation that involves states with a hole localized on the phenyl and states

with a hole localized on the amine end. During the pulse and after it is over, the electronic coherences drive the charge migration with different periods that correspond to the transition frequencies between the states of the cations localized in the two end moieties. There is mainly a 5.9 fs period that corresponds to the transition frequency between the GS (hole on amine) and the two nearly degenerate lowest excited states that have a hole on the amine and a faster period of a 1.35 fs period that corresponds to the beating between the GS and the 6 and 7th excited states. These beatings are reflected in the time dependence of the molecular dipole shown in fig. 5c.

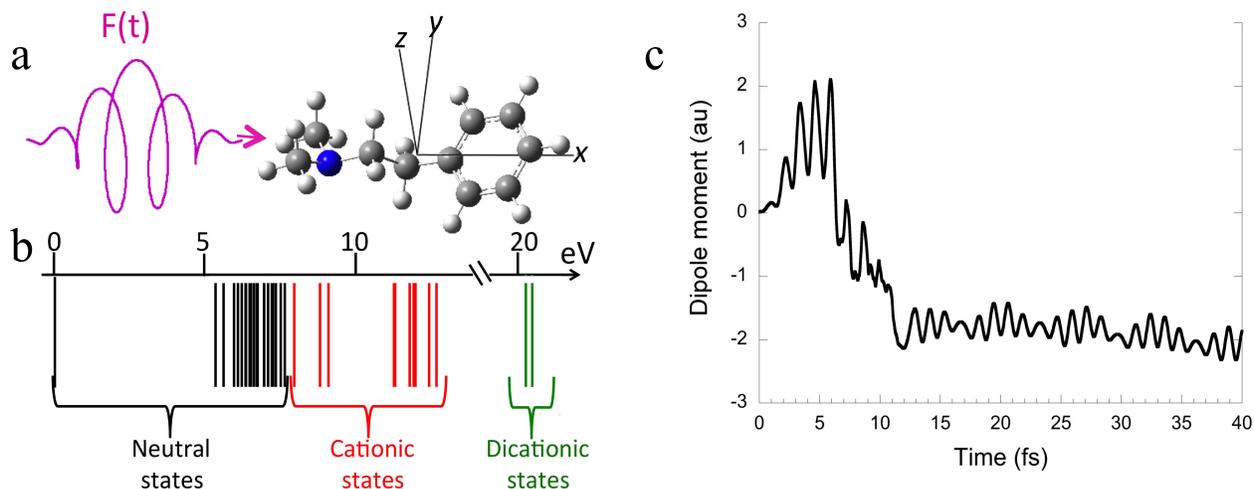


Figure 5. a) PENNA molecule in the molecular frame excited by an IR pulse circularly polarized in the plane perpendicular to the axis of charge migration. b) The electronic manifolds of the neutral, cation and dication included in the dynamical simulations. c) The time dependence of the molecular dipole. Fast (1.35 fs) and slower (5.9 fs) beatings correspond to the transition frequencies between states of the cation localized on different moieties.

By analyzing the angular distribution of the second electron ionized to the dication after a half period of the electric field of the IR laser, it is possible to probe the charge migration in the states of the cation. Preliminary results are shown in Fig.6. Figs. 6a and b show heatmaps of the anisotropy ionization parameter along x , $\alpha_x = (Y_{+x}(t) - Y_{-x}(t)) / (Y_{+x}(t) + Y_{-x}(t))$, plotted as a function of the momentum of the electron ionized and as a function of time during the pulse for the ionization of the neutral to the cation (a) and that of the cation to the dication (b). In Fig.6c, a cut of the anisotropy parameter value is shown for a kinetic energy of the photoelectron of 4.8 eV, for the cation and for the dication, shifted by half a period of the IR pulse, $t_{IR}/2$. The difference between the two curves is shown in fig.6d. When the difference goes through a maximum or a minimum, it means that the two electrons are photoionized in opposite directions. During the pulse, in addition to the period of the IR pulse, the time $-$ dependence of the anisotropy parameter also clearly reflects the fast beating of the electron migration along the x axis, specially in the second half of the pulse. Work is in progress to simulate the momentum correlation between the two electrons, which could be directly compared with the experimental measurements of the Li group.

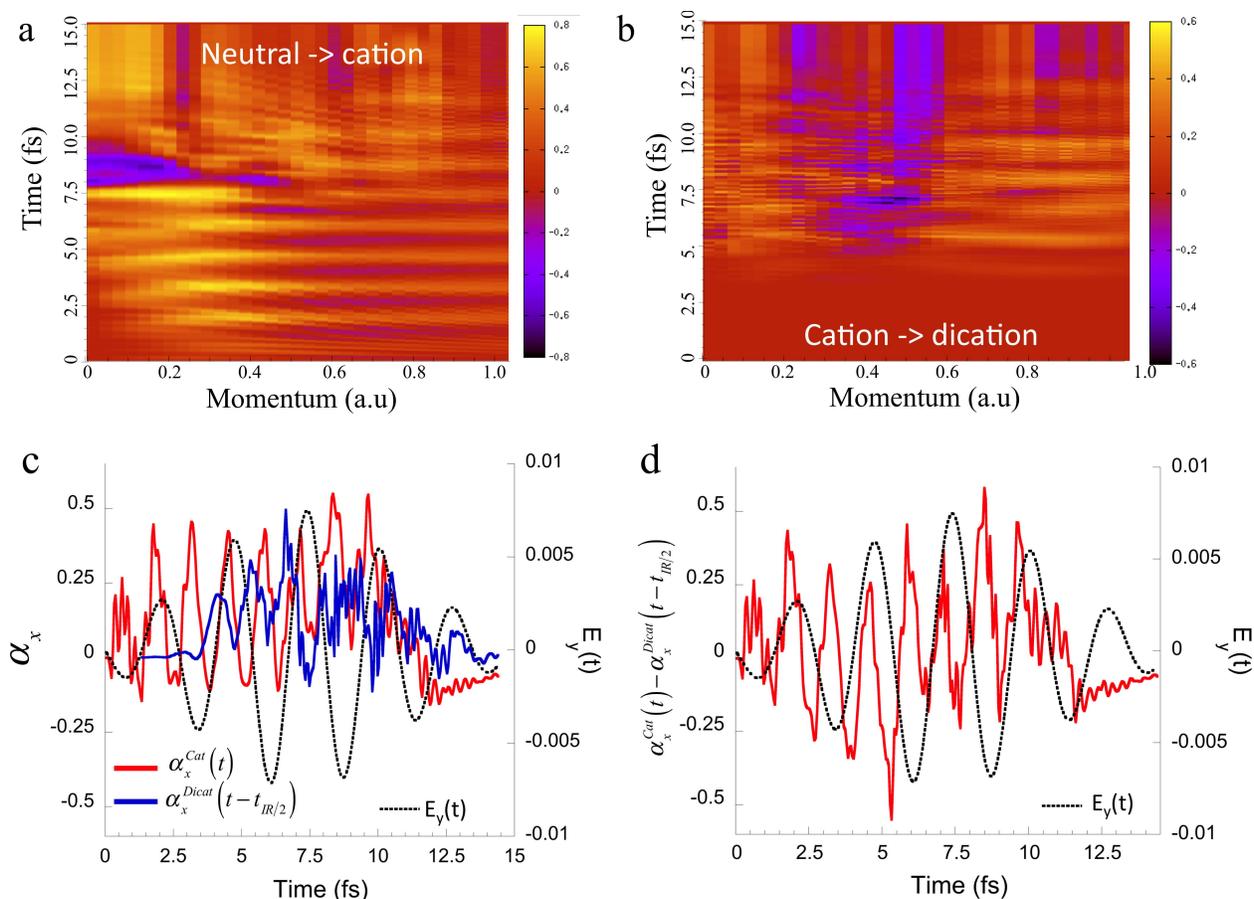


Figure 6 : Top : Heatmaps of the anisotropy ionization parameter, α_x , along the charge migration direction computed as a function of the momentum of the ionized electron and as a function of time for the photoionization of the neutral to the cation (a) and for the photoionization of the cation to the dication (b). Bottom : Cuts of the anisotropy ionization parameter at the electron kinetic energy of 4.8 eV for the cation and the dication (c) and the difference between the two (d). The curve of the dication is shifted by $t_{IR}/2$ to highlight the correlation between the two ionization processes.

In order to investigate the femtosecond nuclear dynamics following photoionization in the cation states of the PENNA, the energetics of the stable conformers, conical intersections (CI) and transition states have been characterized at the SA-CASSCF level for the 3 lowest electronic states (D0, D1 and D2), see figure 7. Two CI were identified in the Franck-Condon (FC) region. One CI between the D0 and D1 and one between D1 and D2. The CI between the D0 and D1 involves the C-C bond of the ethylene bridge and two dihedral angles: the pluckering dihedral angle of the amine (a positively charge amine is planar) and the torsional dihedral angle between the amine and the C-C of the ethylene bridge. Since the hole in these two states is localized on different moieties, passing through the CI is accompanied by a charge transfer. The second CI occurs between D1 and D2. In these two states, the hole is localized on the phenyl. This type of CI involves the quinoic and anti quinoic elongations of the phenyl C-C bonds and no charge transfer. It has been previously characterized in substituted benzene cations [Vacher, M. et al, J. Chem. Phys. 142, 094105, (2015)]. In addition, we have also characterized the transition state on the GS, D0. The barrier height for dissociation is computed to be 0.87 eV.

Ab initio on the fly molecular dynamics simulations was performed on the six states simultaneously with the semi-classical SHARC code [sharc-md.org (2014)], that implements non-adiabatic molecular dynamics simulations using Tully's surface hopping. The non-adiabatic coupling between D_3 , D_4 and D_5 to D_0 , D_1 and D_3 was neglected. Figure 8 shows the relaxation dynamics for an ensemble of 100 trajectories started on D_2 . The computed time scale for the relaxation of D_2 to D_1 is very fast, about 14 fs. The relaxation is essentially sequential, going then from D_1 to D_0 , with a computed time scale for 63 fs. While in D_1 and D_2 , in the FC region, the positive charge is localized on the phenyl moiety, when the population is transferred to the D_0 , the positive charge is localized on the amine group. The computed time scale for charge transfer is compatible with the fs time scale estimated experimentally by Weinkauff and Schlag.[Weinkauff, R. et al, J. Phys. Chem. 100, 18567-18585, (1996)]. Only three trajectories started on D_2 lead to fragmentation. Work in progress aims at implementing a semiclassical approach [M. Ben-Nun and R. D. Levine, Chem. Phys. 201,163(1995)] that goes beyond Ehrenfest dynamics and surface hopping to exploit the effect of electronic coherences on the nuclear dynamics.

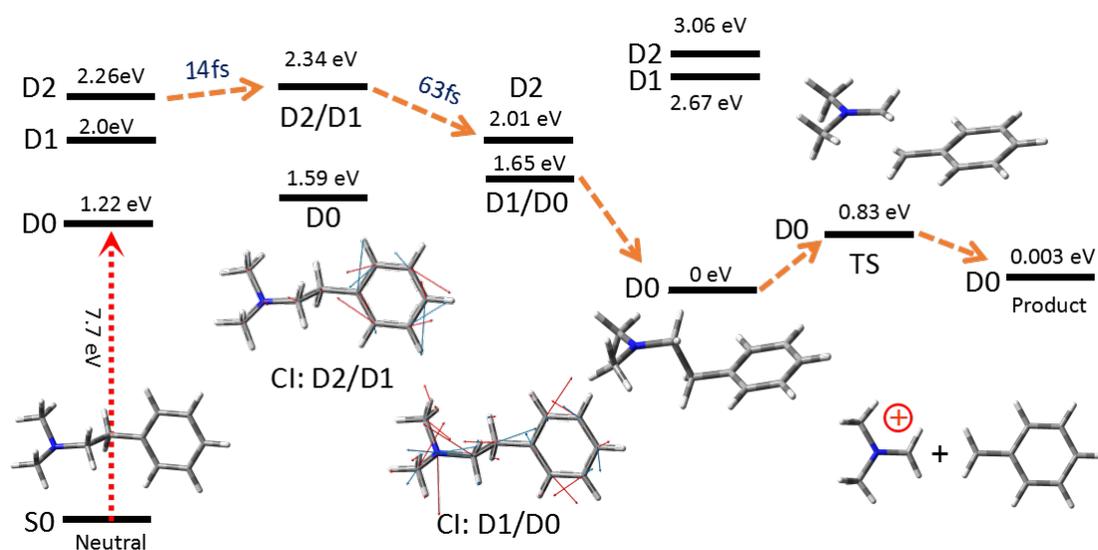


Figure 7. Energetics of the three lowest states of the PENNA cation relevant for the fs dynamics in the PENNA cation following its photoionization to the D_2 state. The computations are carried out at the SA-CASSCF(11,10)/6-31G(d) level, including 6 electronic states. The TS was optimized at the same level for the GS only.

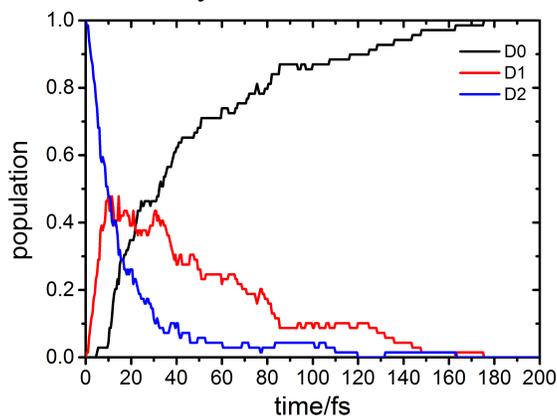


Figure 8. Computed relaxation time scale from an ensemble of 100 trajectories started on D_2 (with ≈ 2 eV of potential energy and ≈ 2 eV of kinetic energy).

Work in progress: plans for the third year and perspectives

In collaboration with the Leone and Neumark group at UC Berkeley we are extending the study of charge migration in N_2 to higher excitation energies where ionization is also possible.

Towards possible experiments of the Li group we are computing both the absorption and the Raman spectrum of attosecond pumped N_2 .

Thus far we have demonstrated that steering the electron density and thereby achieving chemical control is possible in diatomic molecules. We have also simulated spectroscopic experimental responses (photoelectron, transient Raman and absorption spectra) that allow following in time electronic and nuclei motion. Next we have started to investigate nuclear dynamics in larger polyatomic molecules, i.e. on PENNA as reported above and on the cage molecule ABCO ($C_7H_{14}N$), not reported here. During the third year emphasis will be put on continuing the simulation of electronic and nuclear time dependent responses and demonstrating control in larger polyatomic molecules, in collaboration with the Li group.

In summary, we are well on the path towards our stated aim of “*Exploiting Non-equilibrium Charge Dynamics in Polyatomic Molecules to Steer Chemical Reactions*”

In addition we report as follows:

Work is in progress with the Li group to study the momentum electron correlation in the double ionization of the PENNA molecule. The UCLA-ULg group has during the second year investigate fragmentation patterns of the lowest electron states of the cation using Ehrenfest dynamics and work is in progress to use semi-classical approaches that allow for describing the electronic and vibrational coherence essential for implementing control by steering of the electron density.

Work is also in progress in collaboration with the Li and Schlegel groups to analyze the photofragmentation process in the lowest electronic states of the CH_3I cation using momentum coincidence measurements of the photoionized electron and fragments. This experimental probing could also be applied to the fragmentation patterns of the PENNA cation. Further work is in progress in integrating the formalism developed by the UCLA-ULg group to compute photoionization angular distribution and that of the Schlegel group at WSU who developed a methodology to compute angular distribution resulting from strong field ionization over the barrier.

Following scientific discussions during the 1st year meeting in Gaithersburg, a collaboration has started with the group of Nora Berrah (UCONN) on the photoionization of the doped fullerene $Ho_3N@C_{80}$ measured as a function of the intensity of a 30fs 800nm IR fs laser pulse with intensities in the range 0.1 to $5 \cdot 10^{14}$ W/cm². We calculated a large band of Rydberg and SAMO states converging to the IP of the neutral. Unlike in C_{60} , in $Ho_3N@C_{80}$ the SAMO states are optically active which leads to a power law dependence of the ionization yields as a function of the laser intensity different from that observed in C_{60} .

Budget

The UCLA and the ULg groups report that they are spending according to plan and that they will not have any unexpended funds by the end of the second period.

Students or postdocs supported

UCLA: postdoctoral fellow Dr. Jan Smydke with graduate Student Jayanth K. Ajay supported by University funds.

ULg: Post-docs on DoE Funding : Dr. Ksenia Vladimirova from 01/01/2016 to 08/31/2016, Dr. Astrid Nikodem, 01/01/2016-06/30/2016. From ULg funds: Dr. Shoutian Sun from 09/01/2015 to 12/31/2015, Dr. A. Nikodem from 09/01/2015 to 12/31/2015, Dr. B. Mignolet from 09/01/2015 to 31/08/2016.

Papers acknowledging DoE support

1. Ajay, J., et al., *Probing in Space and Time the Nuclear Motion Driven by Nonequilibrium Electronic Dynamics in Ultrafast Pumped N₂*. The Journal of Physical Chemistry A, 2016: p. 10.1021/acs.jpca.6b00165.
2. Nikodem, A., R.D. Levine, and F. Remacle, *Quantum Nuclear Dynamics Pumped and Probed by Ultrafast Polarization Controlled Steering of a Coherent Electronic State in LiH*. The Journal of Physical Chemistry A, 2016: p. 10.1021/acs.jpca.6b00140.
3. Šmydke, J., et al., *Electronic and Nuclear Dynamics for a Non-Equilibrium Electronic State: the Ultrafast Pumping of N₂*. International Journal of quantum Chemistry, 2016: p. accepted.
4. Nikodem, A., R.D. Levine, and F. Remacle, *Controlling coherent quantum nuclear dynamics in LiH by ultra short IR atto pulses*, in *Progress in Ultrafast Laser Science XIII*, K. Yamanouchi, W. Hill, and F. Paulus, Editors. 2016, Springer: New York.
5. Mignolet, B. and F. Remacle, *Time-efficient computation of the electronic structure of the C₆₀ super-atom molecular orbital (SAMO) states in TDDFT*. AIP conference proceedings, 2016: p. accepted.

Conferences presentations

1. Raphael Levine Opening scientific talk at the 20th International conference on quantum Systems in chemistry and Physics, QSCP-XX, Pumping Ultrafast Nonequilibrium Electron Dynamics and Probing by the Induced Nuclear Motion. September 14-17, Varna, Bulgaria.
2. Raphael Levine, Frontier Seminar, An Electronic Time Scale in Chemistry, Wayne State University, October 19, 2015.
3. Raphael Levine, Progress Report, Quantum Nuclear Dynamics Following an Ultrafast Excitation of a NonEquilibrium Electronic State, 2015 Atomic, Molecular, and Optical Sciences Research PI Meeting, October 25-28, 2015.
4. Francoise Remacle, Invited talk, Dynamical studies of Ultrafast Charge Migration in Diatomic and Modular Molecules Probed by Photoelectron Angular Distributions, International Symposium on Ultrafast Intense Laser Science 14, Hawaii, December 8-11, 2015.
5. Francoise Remacle, Invited talk, Dynamical studies of Ultrafast Charge Migration in Diatomic and Modular Molecules, Symposium 'Molecules in laser fields', Orford, May-3-7, 2016, Canada.

6. Françoise Remacle, Invited talk Dynamical studies of Ultrafast Charge Migration in Diatomic and Modular Molecules, Belgian Physical Society Meeting, Ghent (Belgium), May 18, 2016.
7. Benoit Mignolet, Control of electronic dynamics visualized by angularly resolved photoelectron spectra in LiH, PENNA and C60, Computational Chemistry (CC) symposium at the ICCMSE, March 17-20, 2016, Athens, Greece.