Final Technical Report

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Ultrafast Structural Dynamics in Combustion Relevant Model Systems

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I. Program Scope

The research project explored the time resolved structural dynamics of important model reaction system using an array of novel methods that were developed specifically for this purpose. They include time resolved electron diffraction, time resolved relativistic electron diffraction, and time resolved Rydberg fingerprint spectroscopy. Toward the end of the funding period, we also developed time-resolved x-ray diffraction, which uses ultrafast x-ray pulses at LCLS. Those experiments are just now blossoming, as the funding period expired. In the following, the time resolved Rydberg Fingerprint Spectroscopy is discussed in some detail, as it has been a very productive method.

The binding energy of an electron in a Rydberg state, that is, the energy difference between the Rydberg level and the ground state of the molecular ion, has been found to be a uniquely powerful tool to characterize the molecular structure. To rationalize the structure sensitivity we invoke a picture from electron diffraction: when it passes the molecular ion core, the Rydberg electron experiences a phase shift compared to an electron in a hydrogen atom. This phase shift requires an adjustment of the binding energy of the electron, which is measurable. As in electron diffraction, the phase shift depends on the molecular, geometrical structure, so that a measurement of the electron binding energy can be interpreted as a measurement of the molecule's structure.

Building on this insight, we have developed a structurally sensitive spectroscopy: the molecule is first elevated to the Rydberg state, and the binding energy is then measured using photoelectron spectroscopy. The molecule's structure is read out as the binding energy spectrum. Since the photoionization can be done with ultrafast laser pulses, the technique is inherently capable of a time resolution in the femtosecond regime.

For the purpose of identifying the structures of molecules during chemical reactions, and for the analysis of molecular species in the hot environments of combustion processes, there are several features that make the Rydberg ionization spectroscopy uniquely useful. First, the Rydberg electron's orbit is quite large and covers the entire molecule for most molecular structures of combustion interest. Secondly, the ionization does not change vibrational quantum numbers, so that even complicated and large

molecules can be observed with fairly well resolved spectra. In fact, the spectroscopy is blind to vibrational excitation of the molecule. This has the interesting consequence for the study of chemical dynamics, where the molecules are invariably very energetic, that the molecular structures are observed unobstructed by the vibrational congestion that dominates other spectroscopies. This implies also that, as a tool to probe the time-dependent structural dynamics of chemically interesting molecules, Rydberg spectroscopy may well be better suited than electron or x-ray diffraction. With recent progress in calculating Rydberg binding energy spectra, we are approaching the point where the method can be evolved into a structure determination method.

To implement the Rydberg ionization spectroscopy we use a molecular beam based, time-resolved pump-probe multi-photon ionization/photoelectron scheme in which a first laser pulse excites the molecule to a Rydberg state, and a probe pulse ionizes the molecule. A time-of-flight detector measures the kinetic energy spectrum of the photoelectrons. The photoelectron spectrum directly provides the binding energy of the electron, and thereby reveals the molecule's time-dependent structural fingerprint. Only the duration of the laser pulses limits the time resolution. With a new laser system, we have now reached time resolutions better than 100 fs, although very deep UV wavelengths (down to 190 nm) have slightly longer instrument functions. The structural dynamics of molecules in Rydberg-excited states is obtained by delaying the probe ionization photon from the pump photon; the structural dynamics of molecules in their ground state or excited valence states is measured by inducing the dynamics using a near UV laser pulse, and employing a multi-photon ionization scheme via the Rydberg states as a probe process. Thus, the technique is capable of measuring the reaction dynamics in any electronic state of neutral molecules.

II. Results

Electronic curve crossing dynamics in cyclic polyenes

Electronic curve crossing reactions through conical intersections are at work in the opening and closing of hydrocarbon rings containing double bonds. These mechanisms are also in play in the formation of soot during combustion processes. We have continued our studies of the electronic conversion dynamics in cyclopentadienes and cyclohexadienes. Once excited to the optically active $1\ ^1B_2$ surface, these molecules quickly convert to the $2\ ^1A_1$ state. From there, a conical intersection leads down to the molecular ground state, leaving the molecule in either an open or a closed form.

We have succeeded in following this path from the initial excitation to the final product state. Ionization with one, two, or three photon provides views of the molecules in the $1\ ^1B_2$, the $2\ ^1A_1$, and the $1\ ^1A_1$ ground state.

As previously reported, we find that the cyclopentadiene systems cross the electronic states such that the ground state molecular structure is completely recovered (figure 1, 2009 report). Consequently, the binding energies of the Rydberg states that we observe during the curve crossing process do not change with time. In contrast, in the cyclohexadiene systems, we observed that the crossing through the conical intersections

leads to a depletion of the original structure, and the creation of a new structure, i.e. the 1,3,5 hexatrienes.

The sensitivity of the Rydberg spectra coupled with their narrow line shapes even when large amounts of internal energy are present allows us to follow the time-dependent molecular structures. In CHD, we have now been able to observe the structural signature of the ring opening while it happens. When the molecule is ionized out of the ultrashort lived, transient 2 $^1A_1$ state, we observe the Rydberg states that are passed during the ionization transition with the two probe photons. The binding energies of those Rydberg orbits change with delay time, see figure 1: all the sharp peaks are slanting upward with increasing delay time. This constitutes the first truly structural dynamics observation of the ring opening process while it happens!

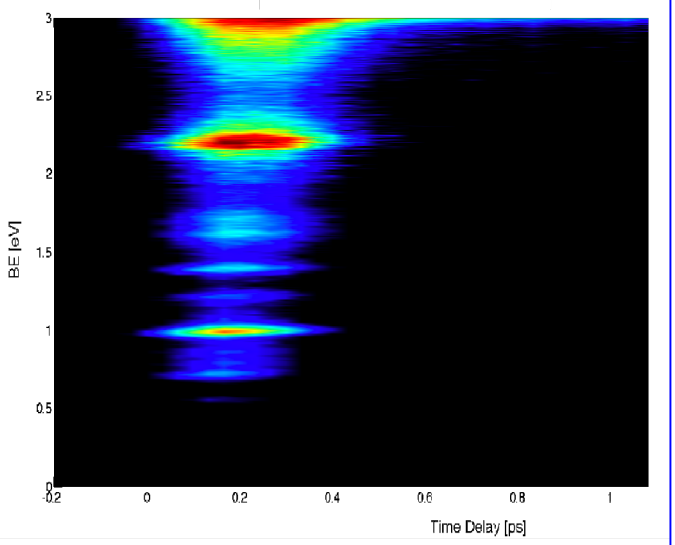

Figure 1: The Rydberg fingerprints of 1,3 cyclohexadiene during the electornic curve crossing. Note that all the Rydberg peaks change their binding energies on an ultrafast time scale, reflecting the structural dynamics.

The analysis of the binding energy spectra uses peak fits of the Rydberg lines. A preliminary analysis shows that the rates of change of the Rydberg electron binding energies depend on the Rydberg orbit. This is understandable as different Rydberg states probe the molecular structures in different ways. Ongoing experimental work seeks to improve the time resolution of the experiment, while the analysis focuses on the deconvolution of the time dependent peak position information.

Ultrafast Dynamics of flexible model systems: formation of a cation-pi bond

Like all chemical reactions, conformeric transitions depend strongly on the potential energy landscape and the temperature at which the system is observed. We seek to explore conformational transformations in model systems under varying experimental conditions. Our measurements can serve as

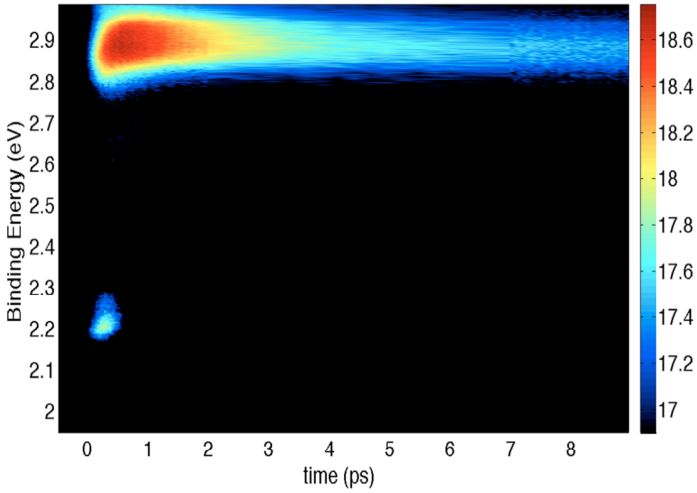

Figure 2: The Rydberg fingerprints of PENNA, showing internal conversion from 3p to 3s on an ultrafast time scale, and time-dependent peak shifts that reflect the structural dynamics.

important benchmarks that can be compared to computational results. From the conformer distributions at the beginning and the end of a reaction one can infer the relative depths of the minima in the potential landscape.

In phenyl ethyl N,N di-methyl amine (PENNA) we observe a rapid internal conversion from 3p (BE=2.2 eV) to 3s (BE = 2.9 eV) (figure 2). The initial conformer distribution in 3p reflects the structures present in the neutral ground state molecules. Rapid planarization of the molecule is evident by the peak shift on a very fast, femtosecond time scale. On a slower, picosecond time scale, we note that the position of the 3s band, observed at around 2.9 eV, is shifting with time. Upon excitation to the Rydberg state, PENNA has two structurally active components: the positive charge at the amine ion core, and the aromatic electrons at the phenyl ring. The interaction between those two moieties drives a structural rearrangement that leads to the formation of a cation-pi bond. It is this structural motion, which competes with a curve crossing to a dissociative state as seen from the rapid and biexponential intensity profile, which leads to the Rydberg electron binding energy shift.

Electronic curve crossing dynamics

Electronic curve crossings through conical intersections are important in the opening and closing of hydrocarbon rings containing double bonds. These mechanisms are very important in the formation of soot during combustion processes. Electrocyclic reactions are a mainstay of organic chemistry and important in energy conversion processes.

The application of the Rydberg photoionization technique to systems with conical intersections has been extremely rewarding. In previous years, we have explored the curve crossing dynamics of cyclopentadiene and cyclohexadiene systems through their conical intersections. Following the Rydberg spectra as a function of time has yielded accurate time constants, which are in the range of 50 to 200 fs, depending on the molecular system. More recently, we have extended these studies to explore how the electronic curve crossing dynamics depends on the electronic energy of the excited state. For this study we use cyclohexadiene as a model system.

While 268 nm excitation into the 1B valence state opens the ring to form hexatriene,

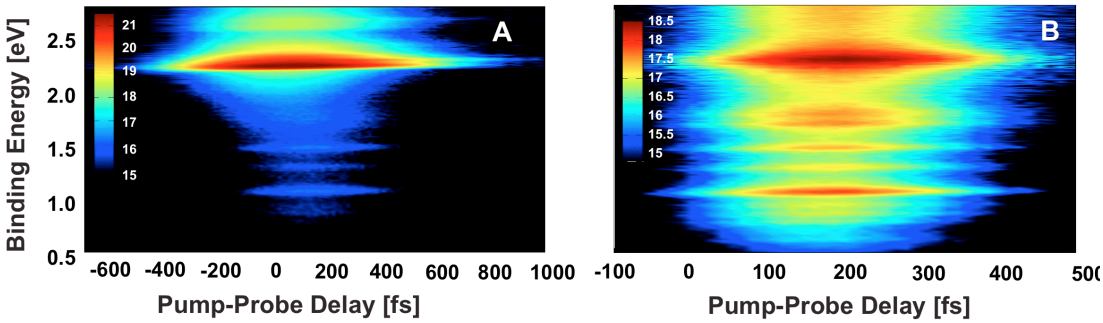

Figure 3: Time-resolved binding energy spectra of 1,3-cyclohexadiene. Part A shows the spectrum with 207 nm excitation, part B represents the result with 268 nm excitation. The color encodes the intensity on a (natural) logarithmic scale.

we have found little evidence for this reaction upon excitation with 207 nm. This is even though the molecule contains 1.36 eV more energy. The analysis of the Rydberg spectra, figure 3, shows that the largest part of the wave packet bypasses the reactive electronic surfaces and goes directly to the ground electronic state.

The difference in the photochemical activity of the states excited at 268 and 207 nm is reflected in the different time dependencies of the Rydberg electron binding energies, figure 4. The photochemically stable state shows a fairly modest variation of the binding energy with delay time, while the opening of the ring is associated with a much larger binding energy shift. Structural distortions associated with 3p-excitation cause a dynamical shift in the p_x- and p_y-binding energies by 10 and 26 meV/ps respectively, whereas after excitation into 1B more severe structural transformations along the ring-opening coordinate produce shifts at a rate of 40 to 60 meV/ps.

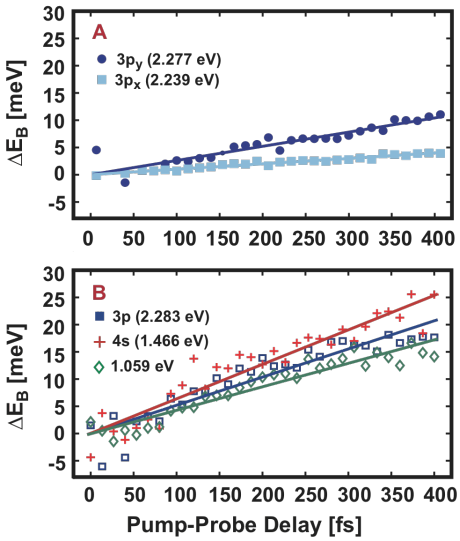

Figure 4: Shifts of peak maxima as a function of time. A: 207 nm + 414 nm ionization: The peak centers of the p_x (light blue squares) and p_y (dark blue circles) signals. Linear fits are included as solid lines in the respective colors. B: 268 m + 400 nm experiment: The shifts of peak centers of the 3p, the 4s and the 1.06 eV peaks as a function of delay time.

It is noteworthy that broadening of the Rydberg lines during the time window of observation is not seen in either experiment. However, the 3p Rydberg signal in the 268 nm experiment is broadened compared to that arising from direct excitation. Previous work has associated the spectral width to dispersion of molecular structure. The lack of observed broadening in the time resolved Rydberg spectra is consistent with the theoretically derived notion that the wavepacket remains well focused during the transition to the ground state. Challenges in the near future include the time and energy deconvoluted analysis of the peak shifts in order to extract the true molecular binding energy variations. These could then be compared to wavepacket dynamics calculations that others have performed.

From these experiments we conclude that the structural dynamics is sensitively dependent on the excited electronic state. This is surprising as one would have expected that the 3p Rydberg state rapidly decays into the lower, reactive valence state. Further, one would have speculated that the 3p state decays first into 3s, which in turn is suspected to evolve into the doubly excited state that opens the ring. None of those mechanisms appear to be at work in CHD. Instead, the molecule finds a very different conical intersection and ends up directly in the ground state, bypassing the reactive channel that is so widely studied by spectroscopists, and used by organic chemists.

Ultrafast Dynamics of flexible model systems

In the past year we have continued our explorations of the structural motions in molecular systems with conformeric degrees of freedom. We have concluded our work on the formation of an intramolecular cation – pi bond, where we watch the formation of this bond in real time. In addition, we finished our studies of the conformeric motions in triethyl amine, where we follow in real time the change of the amine from a pyramidal to a planar structure, which then induces structural motions of the ethyl arms that covers three distinct minima in the potential energy landscape.

We also have extended the study of flexible model systems to include molecular clusters. We observe evidence for the structural rearrangements of the cluster component molecules subsequent to the sudden creation of a charge center, a process that unfolds on a picosecond time scale.

Electronic curve crossing dynamics: faster than a direct dissociation!

The homolytic, photochemical bond cleavage of alkyl nitrites, RONO, to form two radicals, RO· and NO·, has been a model system for a long time. It is well known that when excited by near UV radiation, the dissociation occurs on a femtoseconds time scale and on the S_1 surface. In our experiments, we have excited amyl nitrite ($C_5H_{11}ONO$) at wavelengths of the S_2 absorption, at 266 nm and at 207 nm. The ejection of the NO radical is observed using time-delayed probe pulses and mass spectrometry as well as photoelectron spectroscopy. Figure 5 shows the time dependence of the NO radical fragment upon excitation of amyl nitrite by a 207 nm pulse and ionization of NO by a delayed 414 nm pulse. The splitting, which arises from the kinetic energy of the NO fragment, can be well modeled and yields the kinetic energy of the fragments.

Combining evidence from the kinetic energy, the one-color photoelectron spectra and the time-resolved two-color photoelectron spectra, we concluded that even though the

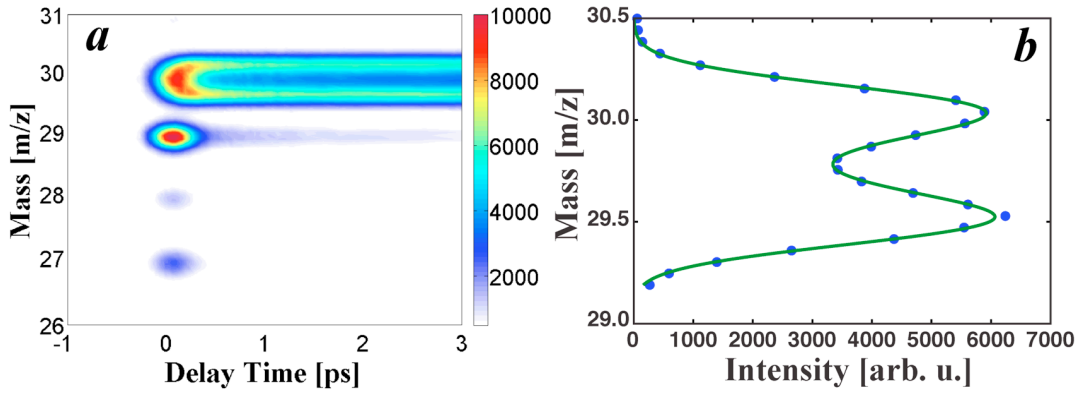

Figure 5: (*a*) Time-resolved mass spectrum in the vicinity of the NO fragment at mass *m/z* 30. The splitting of the NO mass peak at positive delay times arises from the kinetic energy acquired by the NO radicals during the photodissociation. In the contour plot, the 207 nm and 414 nm one-color spectra are subtracted from the time-dependent two-color spectrum. (*b*) The profile of the NO peak in the mass domain at long delay time, averaged from 2 ps to 5 ps. The dots are the experimental data while the solid curve is the fit, yielding the NO kinetic energy.

NO is excited at wavelengths of the electronic transition to S_2, the dissociation does not proceed on the S_2 surface. Instead, the molecule internally converts to the S_1 surface, evidently on a time scale faster than the dissociation on the repulsive S_2 surface!

While our studies on amyl nitrite are quite conclusive, it remains to be seen how general this phenomenon is. Going forward, we plan to study amyl nitrite over a broader wavelength range, as well as other nitrites.

Structural Dynamics in energetic systems: the isomerization of quadricyclane to norbornadiene

The quadricyclene – norbornadiene system is an important model for the isomerization dynamics between highly strained molecules. Using time-resolved photoionization from Rydberg states, we observe the time-dependent structural dynamics and the time-evolving structural dispersion even while the molecule is crossing electronic surfaces. Excitation at 207 nm prepares quadricyclane in the 3p state, which quickly decays to the lower 3s state and isomerizes to norbornadiene. We observe the formation and evolution of the vibrational wavepacket on the Rydberg surface and the internal conversion from the 3p Rydberg states to the 3s state. In that state, quadricyclane isomerizes to norbornadiene with a time constant of τ_2=136(45) fs. The lifetime of the 3p Rydberg state in quadricyclane is τ_1=320(31), and the lifetime of the 3s Rydberg state in norbornadiene is τ_3=394(32). The energy of the quadicyclane Rydberg levels depends on time (figure 2), revealing a structural adjustment even while the molecule is reacting. A careful analysis of the peaks also shows that the width changes with time, suggesting that the wavepacket spreads as the molecule relaxes its structure on the Rydberg surface.

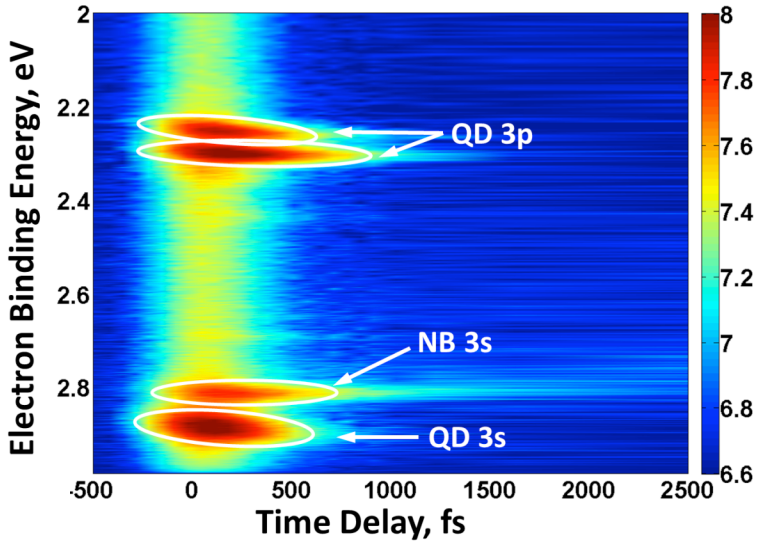

Figure 6: Photoelectron binding energy spectra obtained upon two-color photoionization of quadricyclane with 208 nm pump pulses and 416 nm probe pulses. The one-color contributions to the spectra are subtracted. The initial excitation prepares quadricyclene (QD) in 3p, but it relaxes quickly to the 3s, before converting to norbornadiene.

The electrocyclic ring-opening of 1,3-cyclohexadiene: still full of surprises!

The ring-opening reaction of 1,3-cyclohexadiene (CHD) is a textbook example for a general class of electrocyclic reactions that play an important role in the photochemical opening and closing of organic ring structures. Those reactions are of importance to the understanding of the formation of soot in flames. As a prototypical example, numerous investigations have been made on CHD to elucidate the details of the molecular reaction. Just as we thought we pretty much understand how it works, we have now obtained data that put into question some of this understanding.

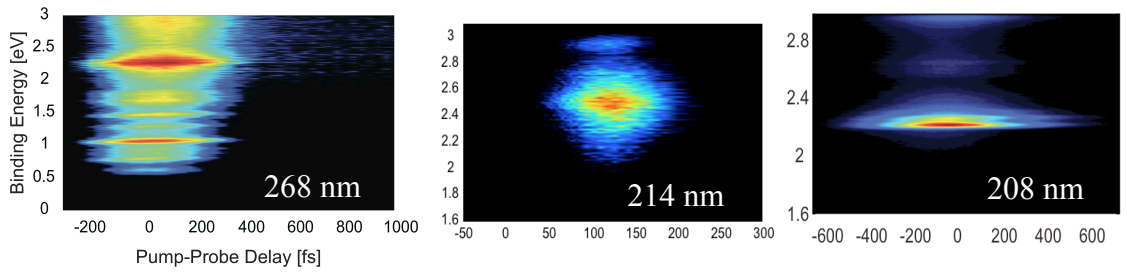

Figure 7: Time-resolved spectra of 1,3-cyclohexadiene excited at 268 nm, 214 nm and 208 nm. The ionization is with a 400 nm pulse at time delays as plotted on the horizontal axis. The binding energy spectrum upon excitation at 268 nm represents the well-known path of the molecule from the B state to the 2A state, followed by a crossing through a conical intersection to the ground state. The spectra at shorter wavelengths are markedly different, suggesting a reaction path distinct from that at 268 nm.

Figure 7 shows the time resolved photoelectron spectra of CHD at several wavelengths across the near UV absorption spectrum of CHD. The longer wavelength is in the general absorption band of the $S_0 \rightarrow S_1$ transition, while at the shorter wavelengths, there are admixtures of other electronic states, notably the Rydberg states. As is clear from Figure 7, the appearance of the time resolved spectra depends dramatically on the excitation energy: rather than being similar albeit with a little more energy, higher excitation energies appear to be associated with a reaction mechanism that does not involve the transition to the 2A state that is so apparent in the spectrum with 268 nm excitation. Ongoing work seeks to better understand the reaction mechanism and the pathway of this interesting molecular model.

Delocalization of a charge in dimethyl piperazine: rate limited by structural motions

Dimethyl piperazine (DMP) is a heterocyclic 6-ring with two nitrogen groups in para position. In its ground electronic state, the nitrogen atoms are too far apart to allow for substantial delocalization of the lone pair electrons. However, in the Rydberg states and the ground state of the ion, the positive charge is delocalized between the two nitrogens. Excitation from the ground state to the Rydberg state involves at first one charge, followed by the delocalization of the charge between the nitrogen charge centers. Figure 8 shows the time-dependend electron binding energy spectrum of the system: upon rapid decay of the initially prepared 3p Rydberg state at 2.2 eV, the molecule arrives at the 3s level partially in a broad peak, from 2.6 to 2.9 eV, that we attribute to a state with a localized charge and partially in a sharp peak near 2.7 eV that likely belongs to the

delocalized charge state. Within the 3s level, we observe a slow reaction from the localized to the delocalized state on a picosecond time scale. While of course the motions of the electrons can be very fast, the rate of the reaction in DMP is confined to the picosecond regime by the structural rearrangements of the ring skeletton that are required to place the system into a geometry that is conducive to charge delocalization.

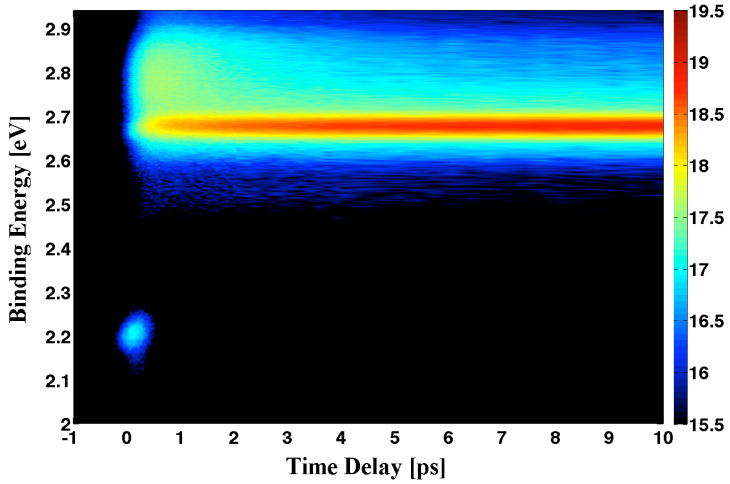

Figure 8: Photoelectron binding energy spectra obtained upon two-color photoionization of dimethyl piperazine with 208 nm pump pulses and 416 nm probe pulses. The one-color contributions to the spectra are subtracted. The initial excitation prepares DMP in 3p (2.2 eV), from where it relaxes quickly to the 3s (2.6 to 2.9 eV).

III. Ongoing research

Even though the funding period came to an end in October 2013, some experiments have continued. In particular, we have been able to achieve spectacular results using x-ray diffraction at LCLS, as was proposed in the renewal application that was unfortunately not funded. These experiments make a strong case for renewed funding and it is hoped that DOE would be open for such a renewal.

IV. Publications resulting from DOE sponsored research (2003 - 2014)

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2. "Self-interaction corrected density functional calculations of molecular Rydberg states," Hildur Gudmundsdóttir, Yao Zhang, Peter M. Weber, and Hannes Jónsson, J. Chem. Phys. **139**, 194102 (2013).
3. "Structural Dynamics and Charge Transfer in Electronically Excited *N,N'*-Dimethylpiperazine" Sanghamitra Deb, Xinxin Cheng and Peter M. Weber, J. Phys. Chem. Lett., 4, 2780−2784 (2013).
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5. "Ultrafast structural and isomerization dynamics in the Rydberg-exited Quadricyclane – Norbornadiene System," Fedor Rudakov and Peter M. Weber, The Journal of Chemical Physics, 136, 1343031 - 7 (**2012**).

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8. "Ultrafast Dynamics of 1,3-Cyclohexadiene in Highly Excited States," Christine C. Bühler, Michael P. Minitti, Sanghamitra Deb, Jie Bao, Peter M. Weber, Journal of Atomic, Molecular, and Optical Physics, Vol. 2011, Article ID 637593, 6 pages, **2011**. doi:10.1155/2011/637593.

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14. "Ultrafast Formation of an Intramolecular Cation-Pi Bond," Joseph C. Bush, Michael P. Minitti and Peter M. Weber. Journal of Photochemistry and Photobiology A: Chemistry 213 **2010**, 70–72.

15. "Ultrafast Curve Crossing Dynamics through Conical Intersections in Methylated Cyclopentadienes," Fedor Rudakov and Peter M. Weber, J. Phys. Chem. A, **2010**, 114 (13), pp 4501–4506.

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