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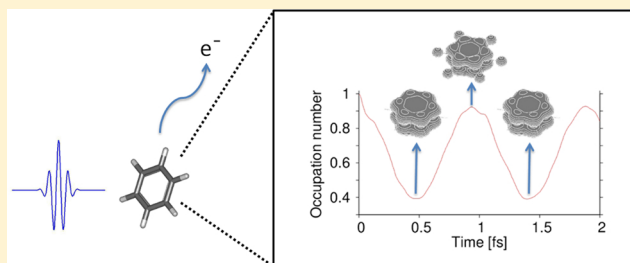
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ABSTRACT: Hole migration is a fascinating process driven by electron correlation, in which purely electronic dynamics occur on a very short time scale in complex ionized molecules, prior to the onset of nuclear motion. However, it is expected that due to coupling to the nuclear dynamics, these oscillations will be rapidly damped and smeared out, which makes experimental observation of the hole migration process rather difficult. In this Letter, we demonstrate that the instantaneous ionization of benzene molecules initiates an ultrafast hole migration characterized by a periodic breathing of the hole density between the carbon ring and surrounding hydrogen atoms on a subfemtosecond time scale. We show that these oscillations survive the dephasing introduced by the nuclear motion for a long enough time to allow their observation. We argue that this offers an ideal benchmark for studying the influence of hole migration on molecular reactivity.



The recent synthesis of very short laser pulses, from a few femtoseconds to a few hundreds of attoseconds duration,¹ enables the real-time observation of charge dynamics in simple and complex molecules that occurs on the atomic time and length scales.² An intriguing example is the so-called hole migration phenomenon, where electron correlation induces ultrafast charge propagation through a complex molecular structure. This process was predicted in the late 1990s³ and since then has been intensively studied theoretically^{4–11}; for a recent review, see ref 12. Hole migration consists of the displacement over the molecular structure of a hole created upon sudden ionization of a molecule due to the coherent population of ionic states. This migration occurs on a very short, femtosecond or even attosecond, time scale and is only driven by the electron correlation. Unlike conventional electron-transfer processes, no nuclear rearrangement is needed. However, due to the coupling between the electronic and nuclear motion, variations in the electronic density may trigger rearrangements in the molecular skeleton. This mechanism (“charge-directed reactivity”¹³) has been proposed¹⁴ as a plausible interpretation for experiments on the fragmentation of biologically relevant molecules.^{15,16} The possibility to initiate purely electronic dynamics that subsequently drive a molecular reaction is a new paradigm for chemistry, offering new means of control beyond stochastically driven reactions and other attempts aiming to exploit the coherence of laser–matter interactions.

Ultrafast charge dynamics triggered by a short XUV pulse has been recently observed in several model polyatomic molecules. The dynamics was induced by vibronic couplings¹⁷ or by direct

coherent superposition of cationic states by a spectrally broad laser pulse.¹⁸ However, despite the fact that correlation-driven hole migration was predicted about 15 years ago, it has not been observed experimentally so far. There are some technical but also fundamental reasons that make the observation of hole migration rather challenging.¹⁹ First of all, the time scale and even the existence of the hole oscillations can be conformer-dependent.²⁰ Consequently, the experimental signal can be smeared out by the presence of several conformers of the molecule in the sample. Even if one is able to overcome this difficulty by selecting a given conformer, the influence of the nuclear motion on the pure electron dynamics may lead to a strong damping of the hole migration signal. Indeed, the hole migration is due to the fact that the ultrafast ionization process creates a hole wave packet by populating several ionic states. Coupling to the nuclear motion will change the relative potential energies of the ionic states and in that way will inevitably introduce decoherence of the electronic wave packet, which will stop the charge oscillations. Usually, the electrons and nuclei move on rather different time scales, and therefore, one would expect that the electronic wave packet will survive long enough for its observation or manipulation. However, this picture only applies when the Born–Oppenheimer approximation is valid, that is, when the coupling between the electronic and nuclear motions is relatively weak. There are many situations though when this coupling is very strong, for

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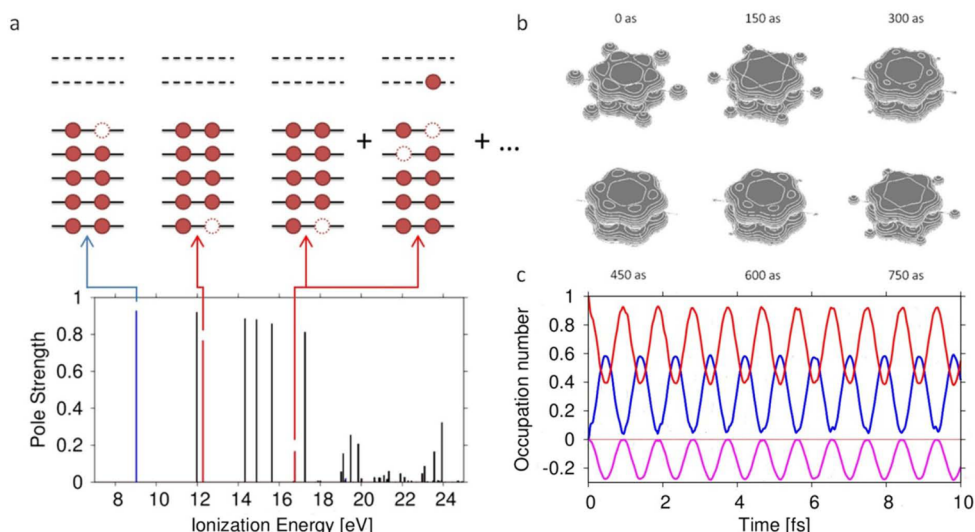


Figure 1. (a) Ionization spectrum of the benzene molecule at the equilibrium geometry obtained using the non-Dyson ADC(3) method. The 1h contributions corresponding to the removal of an electron from orbitals 1e_{1g} and 1a_{2u} are shown in blue and red, respectively. Note that the first two ionic states, corresponding to ionization out of 1e_{1g} (HOMO) and 3e_{2g} (HOMO-1), are doubly degenerate. The electronic nature of some cationic states is schematically presented on the top of the figure (note that in the case of degeneracy, the hole labeled in HOMO-4 will appear in HOMO-2). The main 2h1p configuration of the correlation satellite at 16.7 eV is (1e_{1g})⁻²(1e_{2u}). (b) Snapshots of the time-dependent hole density, defined as the difference between the electronic density of the neutral and the time-dependent electronic density of the ion. The time 0 corresponds to the second maximum in the hole population of orbital 1a_{2u} in panel (c). (c) Time-dependent hole occupations of the orbitals involved in the dynamics triggered by the sudden removal of an electron from the Hartree-Fock orbital 1a_{2u} at the equilibrium geometry. The red line describes the fraction of the hole present in orbital 1a_{2u}, while the blue line corresponds to the occupation of the orbital 1e_{1g} (HOMO); note that the HOMO is doubly degenerate, and an identical contribution (not visible) exists for the second hole opened in orbital 1e_{1g} due to the additional HOMO-LUMO excitation. Correspondingly, the magenta line describes a "negative" hole, that is, an electron occupying the initially empty 1e_{2u} orbital (LUMO), which is also doubly degenerate such that the sum of the total hole population is always equal to 1 (a small difference exists due to weak population of other orbitals).

example, when conical intersections (CIs) between the electronic states appear.^{21,22} The onset of the influence of a CI onto the dynamics can be very fast, leading to a rather quick decoherence of the initial purely electronic wave packet. Whether or not the pure electronic hole dynamics can survive the influence of the nuclear motion depends, therefore, on the respective time scales and strength of the coupling between the electronic and the nuclear degrees of freedom.

In this Letter, we show that the benzene molecule has the needed properties that allow overcoming these constraints. It can be easily introduced into the gas phase and naturally exists in only one conformation. As the building block of the polycyclic aromatic hydrocarbons (PAHs), the benzene molecule often serves as a prototype for studying these very important species. Here, we show that the ionization out of a specific valence orbital of benzene will trigger a robust attosecond hole migration process that, despite the ultrafast nuclear dynamics, survives more than 10 fs, making the benzene molecule a good candidate for experimental studies.

Let us start our discussion by analyzing the ionization spectrum of the benzene molecule at its equilibrium geometry. For computing the ionization spectrum, we used the non-Dyson third-order algebraic diagrammatic construction ADC(3) scheme²³ to represent the one-particle Green's function using the convenient Hartree-Fock orbitals as a one-particle basis. The equilibrium geometry of the benzene molecule was obtained at the B3LYP²⁴/cc-pVDZ²⁵ level using the Gaussian package,²⁶ giving very good agreement with the experimental values for the geometry and vibrational frequencies.^{27,28} The resulting ionization spectrum is shown in Figure 1a. Each line in the spectrum represents an ionic

eigenstate and is located at the corresponding ionization energy. The height of the line (i.e., the pole strength) reflects the contribution of the one-hole (1h) configurations to the ionic states (each 1h configuration accounts for the removal of an electron from a particular molecular orbital). In the absence of electron correlation, one would obtain a series of lines with a height of 1 for each occupied molecular orbital. Electron correlation manifests itself as a mixing of different 1h configurations in individual ionic states as a reduction of the line height (with the "missing" part reflecting the contribution of two-hole-one-particle (2h1p) and higher configurations) and, related with the latter, as the appearance of additional (satellite) lines in the spectrum. A 2h1p configuration describes removal of an electron from a particular orbital accompanied by the excitation of another electron to an initially unoccupied orbital. For an indepth analysis of ionization spectra computed by many-body methods, the reader is referred to ref 29.

The calculated spectrum is shown up to 24 eV and therefore predicts all of the states that can be populated when the benzene molecule is ionized by a 24 eV photon. We see that the spectrum consists of two regions. The first region (up to 18 eV) contains mainly 1h states, while the second region (above 18 eV) is composed of states with a large contribution of 2h1p configurations. An interesting feature in the first region is the two states depicted in red in the figure, a main state at 12.30 eV and its energetically distant shakeup (or satellite state) at 16.72 eV. We note in passing that the existence of this correlation satellite has been proven experimentally³⁰ and discussed in some detail theoretically.³¹ The 1h part of these states describes the removal of an electron from the 1a_{2u} (π) Hartree-Fock molecular orbital, which corresponds to the HOMO-2 (note

that HOMO and HOMO–1 are doubly degenerate). Here and in the following, the standard D_{6h} symmetry notations are used. Instantaneously removing an electron from the $1a_{2u}$ orbital thus coherently populates these two ionic states, triggering in that way a charge migration with a time scale governed by the energy difference between the states. We have propagated the electronic wave packet resulting from the sudden ionization out of the $1a_{2u}$ orbital at the equilibrium geometry using the multielectron wave packet propagation method.³² The method consists of direct propagation of the initial state with the full many-body cationic Hamiltonian of the system, constructed using the non-Dyson ADC(3) scheme. The resulting time-dependent hole occupations of the orbitals involved in the dynamics are reported in Figure 1b. An ultrafast transfer of population from the initial hole created in the orbital $1a_{2u}$ to the $1e_{1g}$ orbital (which is the doubly degenerate HOMO) and a simultaneous excitation from the HOMO ($1e_{1g}$) to the doubly degenerate LUMO ($1e_{2u}$) occur. The oscillations have a period of 935 as, which corresponds to the energy difference of 4.42 eV between the main state and its satellite. Snapshots of the hole density (defined as the difference between the electronic density of the neutral and the time-dependent electronic density of the ion) along one full oscillation period are shown in Figure 1b. One can see that the charge oscillations correspond to a variation of the hole density in and out of the carbon ring (note that the hole periodically appears on and disappears from the surrounding H atoms). Therefore, the hole dynamics corresponds to a spatial “breathing motion” of the hole density on the attosecond time scale.

Despite the fact that this hole migration is extremely fast, nuclear motion, especially of the H atoms, can occur on time scales that might efficiently erase this remarkable dynamics in a realistic experimental situation. In order to investigate the effect of the nuclear motion on the purely electronic dynamics, vibrational frequencies were computed at the B3LYP/cc-pVDZ level, using the Gaussian package, and the change of the ionization spectrum along the 30 normal coordinate modes was investigated (note that 10 modes are degenerate, and therefore, only 20 modes are discussed). In order to emphasize the effects of the vibrations, the calculations of the ionization spectrum were performed for large displacements, up to $q_i = 0.4$, for each one of the 30 normal modes (q_i is the normal coordinate). Our analysis shows that depending on their influence on the ionization spectrum and, in particular, on the states populated by the removal of an electron from orbital $1a_{2u}$, the normal modes can be grouped in three different categories (see Table 1): (a) modes along which the ionization spectrum changes significantly, with the emergence of additional states correlated with the hole in the $1a_{2u}$ orbital (Table 1a), (b) a mode along which the intensity of the $(1a_{2u})^{-1}$ satellite strongly diminishes and even disappears (Table 1b), and (c) modes along which the spectrum varies only slightly (Table 1c). Selected spectra presenting some typical cases at the maximum displacement studied ($q_i = 0.4$) are shown in Figure 2 together with the evolution of the corresponding orbital occupations.

Let us now analyze in detail the dynamics in these three different cases. In the first case, we have four vibrational normal modes along which the nature of the electronic states of the ion change drastically, leading even to the appearance of new satellites containing the $(1a_{2u})^{-1}$ contribution (see Figure 2a and b). This, of course, will substantially change the charge migration dynamics, introducing new oscillation periods and leading to beatings in the hole oscillations (see the evolution of

Table 1. Normal Vibrational Modes of the Benzene Molecule

symmetry	freq [cm^{-1}]
(a) Category 1	
b_{2g}	723
e_{2g}	1646
e_{2u}	414
e_{2u}	987
(b) Category 2	
b_{2u}	1358
(c) Category 3	
a_{1g}	1020
a_{1g}	3202
a_{2g}	1365
a_{2u}	690
b_{1u}	1014
b_{1u}	3164
b_{2g}	1022
b_{2u}	1163
e_{1g}	866
e_{1u}	1060
e_{1u}	1507
e_{2g}	3191
e_{2g}	618
e_{2g}	1187
e_{2g}	3175

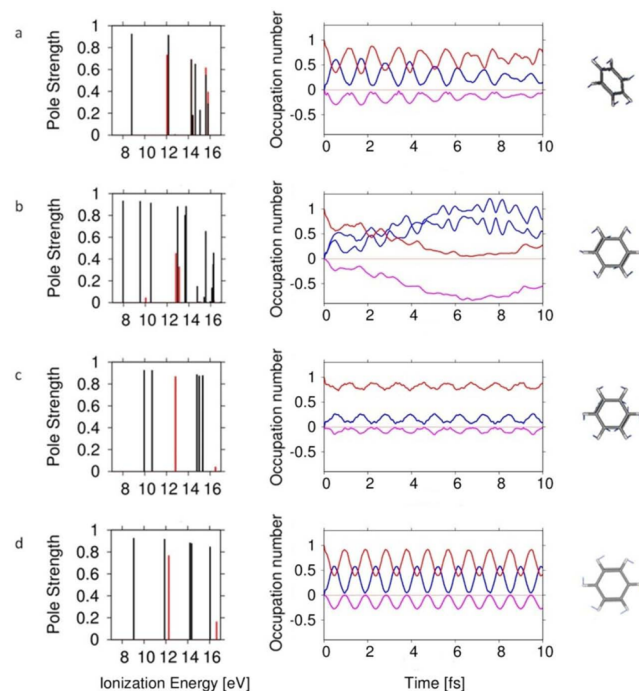


Figure 2. Ionization spectrum of the benzene molecule obtained with the non-Dyson ADC(3) method for a displacement of $q_i = 0.4$ for four representative normal modes (shown on the right) and the corresponding time-dependent hole occupations. The normal modes displayed are (a) b_{2g} at 723 cm^{-1} , (b) e_{2g} at 1646 cm^{-1} , (c) b_{2u} at 1358 cm^{-1} , and (d) a_{2g} at 1365 cm^{-1} . The color code of the 1h configurations and the corresponding occupations are the same as those in Figure 1.

the hole occupations shown in Figure 2a and b). As a result, the hole migration process will be masked along these four normal

modes. As we mentioned above, along the normal mode of the second category, the movement of the nuclei induces a collapse of the satellite state, and at the maximum displacement studied, the $(1a_{2u})^{-1}$ configuration contributes practically only to a single ionic eigenstate (see Figure 2c). In this case, the nuclear dynamics will quench the pure electronic hole migration. In the last category of normal modes, the nuclear motion only slightly affects the cationic states, mainly changing a little the energy difference between the two cationic states involved in the charge migration (see Figure 2d). A closer look at the variations in this energy difference shows that the change in the period with respect to the equilibrium situation is between 3 and 131, as for all of the modes considered, or on average about 41, which is about a 4% change in the period of the hole migration compared to the one at the equilibrium geometry. The above analysis shows that only 5 out of 20 studied vibrational modes (b_{2u} at 1358 cm^{-1} , b_{2g} at 723 cm^{-1} , e_{2g} at 1646 cm^{-1} , e_{2u} at 414 cm^{-1} , and e_{2u} at 987 cm^{-1}) significantly quench or alter the charge dynamics that we want to observe.

In order to simulate the overall effect of the vibrational motion, the hole propagation has been computed and averaged over all normal modes; propagation has been made with frozen nuclei at fixed deformations of $0.1q_i$, $0.2q_i$, $0.3q_i$, and $0.4q_i$. We assumed a Boltzmann distribution for the population of vibrational modes and used the force constant to determine the maximum oscillation amplitude for each mode. In the calculation, we assumed a vibrational temperature of 3000 K, at which 11 normal modes have a maximum oscillation amplitude in excess of 0.05 (e_{2u} at 414 cm^{-1} , e_{2g} at 618 cm^{-1} , a_{2u} at 690 cm^{-1} , b_{2g} at 723 cm^{-1} , e_{1g} at 866 cm^{-1} , e_{2u} at 987 cm^{-1} , b_{2g} at 1022 cm^{-1} , e_{1u} at 1060 cm^{-1} , b_{2u} at 1163 cm^{-1} , e_{2g} at 1187 cm^{-1} , and a_{2g} at 1365 cm^{-1}), and no mode has a maximum amplitude in excess of 0.2. We chose to use a temperature 1 order of magnitude higher than the initial temperature of the molecule generated in an experiment (few hundreds of Kelvin) to account for the vibrational excitation that accompanies the ionization. The result of the calculation is presented in Figure 3,

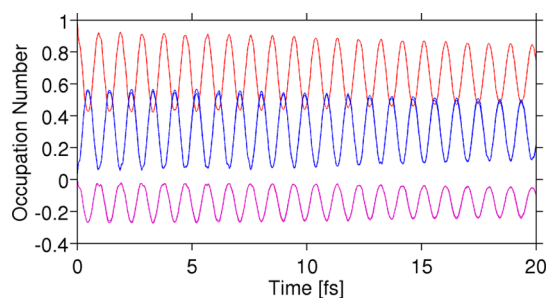


Figure 3. Hole migration dynamics averaged over 30 normal modes (the color code is the same as that in Figure 1). The contribution of each mode is weighted by the statistical contribution of its energy at 3000 K (see the text for further details).

showing a very weak damping of the hole oscillations over the first 20 fs. Therefore, taking into account all vibrational modes, the charge migration is predicted to be robust at this temperature. The fact that the electron dynamics survives at this relatively high temperature is striking and shows that the benzene can serve as a benchmark for observing and studying the hole migration phenomenon.

Let us now discuss the effect of CIs. The presented analysis was based on the changes that the nuclear motion induces to

the cationic states involved in the hole migration. However, the nuclear motion can furthermore strongly couple the electronic states at CIs, where population can be transferred from one state to another. In other words, even if the initial ionization populates several states, triggering in that way a hole migration, the population can funnel out quickly from these states through CIs. The nonadiabatic dynamics involving the first five electronic states of the benzene radical cation have previously been studied^{33,34} with the help of nuclear wave packet propagation using the MCTDH algorithm³⁵ (using the Heidelberg implementation³⁶) within the (quasi)-diabatic picture and the linear vibronic coupling approximation. The calculations have revealed that de-excitation of these states through CIs to the cationic ground state occurs within a few tens of femtoseconds.

To simulate the mutual influence of the electronic and nuclear motion, one needs to perform coupled electron–nuclear dynamics calculations. Unfortunately, a full quantum treatment of both nuclei and electrons is currently out of reach for polyatomic systems. A possible way to overcome this limitation is the semiclassical method based on Ehrenfest dynamics, which has been recently proposed by Robb and co-workers.^{37,38} This method was used to study the influence of the CI on the dynamics initiated by the ionization out of the HOMO of benzene and revealed also a time scale of a few tens of femtoseconds. On the basis of these results for the nonadiabatic dynamics in benzene, we anticipate that the charge migration will continue, nearly unaffected, for at least 10 fs, that is, the hole will display more than 10 oscillation periods before the population is transferred to other low-lying states, not involved in the ultrafast charge migration.

To summarize, ultrafast hole dynamics can be observed experimentally if the vibration of the molecule does not have a strong influence on the topology of the ionization spectrum and if the period of the hole oscillations is shorter than the lifetime of the states that are vibronically coupled. We have demonstrated that the benzene molecule offers such an opportunity due to the availability of a robust and well-defined shakeup state that is populated as a result of the correlation effects.

Before concluding, let us briefly discuss a possible scheme for an experimental observation of the studied hole migration process. In order to observe these dynamics, we propose a pump–probe experiment. A short XUV pulse with a maximum energy of 17 eV should populate all of the cationic states below this energy, including the states that are responsible for the ultrafast hole migration. Ideally, the dynamics would be revealed by measuring directly the time-dependent population of the HOMO–2 and LUMO by using electron spectroscopy, which is however not an easy task. As an alternative, we propose to measure variations in the fragmentation pattern of the molecule. Because in this particular migration process the hole density varies around the H atoms, one may expect the hole migration to affect the probability for IR-induced H-loss. H-loss is a major decay channel in benzene³⁹ and can be induced by nonlinear IR excitation⁴⁰. Therefore, we propose that following the XUV ionization step, the dynamics is probed by means of the absorption of a few IR photons (using a short CEP stable pulse where excitation would be confined within a half-cycle⁴¹).

Finally, we note that the similar properties that all PAH molecules possess suggests that other members of this molecular family may also be suitable for experimental studies

of the kind discussed here. Consequently, the benzene molecule appears as a prototype and building block for hole migration investigations in increasingly complex molecules. We hope that our study will stimulate specific efforts to observe and study correlation-driven hole dynamics.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Krausz, F.; Ivanov, M. Y. Attosecond Physics. *Rev. Mod. Phys.* **2009**, *81*, 163–234.
- (2) Lépine, F.; Ivanov, M. Y.; Vrakking, M. J. J. Attosecond Molecular Dynamics: Fact or Fiction? *Nat. Photonics* **2014**, *8*, 195–204.
- (3) Cederbaum, L. S.; Zobeley, J. Ultrafast Charge Migration by Electron Correlation. *Chem. Phys. Lett.* **1999**, *307*, 205–210.
- (4) Breidbach, J.; Cederbaum, L. S. Migration of Holes: Formalism, Mechanisms, and Illustrative Applications. *J. Chem. Phys.* **2003**, *118*, 3983–3996.
- (5) Hennig, H.; Breidbach, J.; Cederbaum, L. S. Electron Correlation as the Driving Force for Charge Transfer: Charge Migration Following Ionization in *N*-Methyl Acetamide. *J. Phys. Chem. A* **2005**, *109*, 409–414.
- (6) Kuleff, A. I.; Lünemann, S.; Cederbaum, L. S. Electron-Correlation-Driven Charge Migration in Oligopeptides. *Chem. Phys.* **2013**, *414*, 100–105.
- (7) Kuleff, A. I.; Cederbaum, L. S. Radiation Generated by the Ultrafast Migration of a Positive Charge Following the Ionization of a Molecular System. *Phys. Rev. Lett.* **2011**, *106*, 053001/1–053001/4.
- (8) Periyasamy, G.; Levine, R. D.; Remacle, F. Electronic Wave Packet Motion in Water Dimer Cation: A Many Electron Description. *Chem. Phys.* **2009**, *366*, 129–138.
- (9) Mignolet, B.; Levine, R. D.; Remacle, F. Localized Electron Dynamics in Attosecond-Pulse-Excited Molecular Systems: Probing the Time-Dependent Electron Density by Sudden Photoionization. *Phys. Rev. A* **2012**, *86*, 053429/1–053429/8.
- (10) Kuš, T.; Mignolet, B.; Levine, R. D.; Remacle, F. Pump and Probe of Ultrafast Charge Reorganization in Small Peptides: A Computational Study through Sudden Ionizations. *J. Phys. Chem. A* **2013**, *117*, 10513–10525.
- (11) Cooper, B.; Averbukh, V. Single-Photon Laser-Enabled Auger Spectroscopy for Measuring Attosecond Electron–Hole Dynamics. *Phys. Rev. Lett.* **2013**, *111*, 083004/1–083004/4.
- (12) Kuleff, A. I.; Cederbaum, L. S. Ultrafast Correlation-Driven Electron Dynamics. *J. Phys. B* **2014**, *47*, 124002/1–124002/12.
- (13) Remacle, F.; Levine, R. D.; Ratner, M. A. Charge Directed Reactivity: A Simple Electronic Model, Exhibiting Site Selectivity, for the Dissociation of Ions. *Chem. Phys. Lett.* **1998**, *285*, 25–33.
- (14) Lünemann, S.; Kuleff, A. I.; Cederbaum, L. S. Ultrafast Charge Migration in 2-Phenylethyl-*N,N*-dimethylamine. *Chem. Phys. Lett.* **2008**, *450*, 232–235.
- (15) Weinkauff, R.; Aicher, P.; Wesley, G.; Grotemeyer, J.; Schlag, E. W. Femtosecond versus Nanosecond Multiphoton Ionization and Dissociation of Large Molecules. *J. Phys. Chem.* **1994**, *98*, 8381–8391.
- (16) Lehr, L.; Horneff, T.; Weinkauff, R.; Schlag, E. W. Femtosecond Dynamics after Ionization: 2-Phenylethyl-*N,N*-dimethylamine as a Model System for Nonresonant Downhill Charge Transfer in Peptides. *J. Phys. Chem. A* **2005**, *109*, 8074–8080.
- (17) Timmers, H.; Li, Z.; Shivaram, N.; Santra, R.; Vendrell, O.; Sandhu, A. Coherent Electron Hole Dynamics near a Canonical Intersection. *Phys. Rev. Lett.* **2014**, *113*, 1130031–1130034.
- (18) Calegari, F.; Ayuso, D.; Trabattini, A.; Belshaw, L.; De Camillis, S.; Anumula, S.; Frassetto, F.; Poletto, L.; Palacios, A.; Decleva, P.; et al. Ultrafast Electron Dynamics in Phenylalanine Initiated by Attosecond Pulses. *Science* **2014**, *346*, 336–339.
- (19) Leone, S. R.; McCurdy, C. W.; Burgdörfer, J.; Cederbaum, L. S.; Chang, Z.; Dudovich, N.; Feist, J.; Greene, C. H.; Ivanov, M. Y.; Kienberger, R.; et al. What Will It Take to Observe Processes in “Real Time”? *Nat. Photonics* **2014**, *8*, 162–166.
- (20) Kuleff, A. I.; Cederbaum, L. S. Charge Migration in Different Conformers of Glycine: The Role of Nuclear Geometry. *Chem. Phys.* **2007**, *338*, 320–328.
- (21) Worth, G. A.; Cederbaum, L. S. Beyond Born–Oppenheimer: Molecular Dynamics through a Canonical Intersection. *Annu. Rev. Phys. Chem.* **2004**, *55*, 127–158.
- (22) Domcke, W.; Yarkony, D. R.; Köppel, H. *Conical Intersections: Theory, Computations, and Experiment*; World Scientific: Singapore, 2011.
- (23) Schirmer, J.; Trofimov, A. B.; Stelter, G. A Non-Dyson Third-Order Approximation Scheme for the Electron Propagator. *J. Chem. Phys.* **1998**, *109*, 4734–4744.
- (24) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (25) Dunnin, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (26) Frisch, M. J. et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.
- (27) Tamagawa, K.; Ijima, T.; Kimura, M. Molecular Structure of Benzene. *J. Mol. Struct.* **1976**, *30*, 243–253.
- (28) Pulay, P.; Fogarasi, G.; Boggs, J. E. Force Field, Dipole Moment Derivatives, and Vibronic Constants of Benzene from a Combination of Experimental and Abinitio Quantum Chemical Information. *J. Chem. Phys.* **1981**, *74*, 3999–4014.
- (29) Cederbaum, L. S.; Domcke, W.; Schirmer, J.; von Niessen, W. Correlation Effects in the Ionization of Molecules: Breakdown of the Molecular Orbital Picture. *Adv. Chem. Phys.* **1986**, *65*, 115–159.
- (30) Masuda, S.; Aoyama, M.; Ohno, K.; Harada, Y. Observation of Unusually Enhanced Satellite Band in Penning-Ionization Electron Spectra of Benzene and Toluene. *Phys. Rev. Lett.* **1990**, *65*, 3257–3260.
- (31) Weikert, H.-G.; Cederbaum, L. S. On the Satellite Structure Accompanying the Ionization of Benzene. *Chem. Phys. Lett.* **1995**, *237*, 1–6.
- (32) Kuleff, A. I.; Breidbach, J.; Cederbaum, L. S. Multielectron Wave-Packet Propagation: General Theory and Application. *J. Chem. Phys.* **2005**, *123*, 044111/1–044111/10.
- (33) Döschner, M.; Köppel, H.; Szalay, P. G. Multistate Vibronic Interactions in the Benzene Radical Cation. I. Electronic Structure Calculations. *J. Chem. Phys.* **2002**, *117*, 2645–2656.
- (34) Köppel, H.; Döschner, M.; Bâldea, I.; Meyer, H.-D.; Szalay, P. G. Multistate Vibronic Interactions in the Benzene Radical Cation. II. Quantum Dynamical Simulations. *J. Chem. Phys.* **2002**, *117*, 2657–2671.
- (35) Beck, M. H.; Jäckle, A.; Worth, G. A.; Meyer, H.-D. The Multiconfiguration Time-Dependent Hartree (MCTDH) Method: A Highly Efficient Algorithm for Propagating Wavepackets. *Phys. Rep.* **2000**, *324*, 1–105.
- (36) MCTDH. <http://www.pci.uni-heidelberg.de/cms/mctdh.html> (2014).
- (37) Mendive-Tapia, D.; Vacher, M.; Berrpark, M. J.; Robb, M. A. Coupled Electron–Nuclear Dynamics: Charge Migration and Charge Transfer Initiated near Conical Intersection. *J. Chem. Phys.* **2013**, *139*, 044110/1–044110/12.
- (38) Vacher, M.; Berrpark, M. J.; Robb, M. A. Communication: Oscillating Charge Migration Between Lone Pairs Persists Without Significant Interaction with Nuclear Motion in the Glycine and Gly-

Gly-NH-CH₃ Radical Cations. *J. Chem. Phys.* **2014**, *140*, 2011021–2011025.

(39) Gridelet, E.; Lorquet, A. J.; Loch, R.; Lorquet, J. C.; Leyh, B. Hydrogen Atom Loss from Benzene Cation. Why Is the Kinetic Energy Release so Large. *J. Phys. Chem. A* **2006**, *110* (27), 8519–8527.

(40) Talebpour, A.; Bandrauk, A. D.; Chin, S. L. Fragmentation of Benzene in an Intense Ti: Sapphire Laser Pulse. *Laser Phys.* **2000**, *10*, 210–215.

(41) Alnaser, A. S.; Kübel, M.; Siemering, R.; Bergues, B.; Kling, N. G.; Betsch, K. J.; Deng, Y.; Schmidt, J.; Alahmed, Z. A.; Azzeer, A. M.; et al. Subfemtosecond Steering of Hydrocarbon Deprotonation Through Superposition of Vibrational Modes. *Nat. Commun.* **2013**, *5*, 3800/1–3800/6.