The Ultrafast Structural Pathway of Charge Transfer in Tetramethylethylene-ридiamine

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ABSTRACT. We have explored the ultrafast molecular structural dynamics associated with charge transfer in $N, N, N', N'$-tetramethylethylenediamine using Rydberg Fingerprint Spectroscopy in conjunction with density functional theory with the self-interaction correction. Excitation at 239 nm prepares the molecule in the Franck-Condon region of the 3s state with the charge localized on one of the two amine groups. As seen from the time-dependent Rydberg electron binding energies, the pathway of the rapidly ensuing dynamics leads through several structurally distinct conformational forms with various degrees of charge localization before reaching the fully charge delocalized structure on a picosecond time scale. At several steps along the reaction path, the transient structures are identified through a comparison of the spectroscopically observed electron binding energies with values computed using density functional theory. The molecular structure is seen to evolve dynamically from an initially folded conformer to the stretched form that supports charge delocalization, before an equilibrium sets in with forward and backward time constants of 1.19 (0.14) ps and 2.61 (0.31) ps, respectively.

TOC GRAPHICS

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Understanding the structural nuclear and electron motions during chemical reactions is important for designing novel catalysts, exploring new reaction paths and selectively controlling reactions on molecular level. Among the many types of chemical reactions, those involved with charge transfer (CT) are especially important because of their relevance to many reactions in chemical synthesis, to biological systems such as DNA and proteins, and to the mechanistic processes in nanoscale devices.\textsuperscript{1,2,3,4} To monitor molecular dynamics in real time, pump-probe techniques\textsuperscript{2} have been widely used in conjunction with traditional spectroscopic techniques such as absorption spectroscopy, Raman scattering, and photoelectron spectroscopy. With recent progress in the generation of ultrafast pulsed, intense X-ray beams and ultrafast electron sources, time-resolved gas phase X-ray and electron diffractions also have great potential to directly map molecular structures in real time.\textsuperscript{5,6,7} Despite these advances in determining real-time molecular structures, the observation of structural dynamics at high effective temperature, where chemical reactions often proceed, remains challenging because of the vibrational congestion and structural dispersion. This problem is particularly pertinent for structurally flexible molecules that often arise as intermediates during chemical reactions. Additionally, the large facilities often associated with ultrafast, intense X-ray or electron beams further limit their applications. In contrast, time-resolved Rydberg Fingerprint Spectroscopy (RFS), in conjunction with the recently developed density functional theory with the self-interaction correction (DFT-SIC), has proven its ability to capture the structural dynamics of hot and floppy molecules. We applied this method to search for structural transients in the charge delocalization dynamics of $N, N, N', N'$-tetramethylethylenediamine (TMEDA). We discovered both dramatic and subtle structural
changes that reveal the molecular reaction path via distinct conformational forms on a sub-picosecond time scale.

RFS takes advantage of the sensitivity of the binding energy (BE) of a Rydberg electron to both the structure and the charge distribution of a molecular ion core, coupled with its insensitivity to vibrational excitations. The time-resolved measurement of the BE has emerged as an effective tool to probe molecular structural dynamics, such as the hydrogen transfer process in large molecular clusters, the conformational dynamics in hot flexible aliphatic molecules, and the charge transfer dynamics in a bi-functional molecule, and several systems with multiple ionization centers. The molecular ion core of a Rydberg state closely resembles the molecular cation because the distant Rydberg electron has a weak effect on the chemical bonding of the core. Since the ejection of a photoelectron is fast compared to nuclear motions, the photoelectron spectra reflect the molecular structure at the time the electron is ejected. The structural dynamics is observed by inserting a time delay between the excitation of the molecule and its ionization. To identify specific molecular transients, we compute the binding energies of potential structures using DFT-SIC and compare the computational results to the observed spectra.

TMEDA and it derivatives have previously served as molecular models to investigate electron lone pair interactions and charge delocalization. In its ground state, TMEDA has negligible lone pair interaction as evidenced by photoionization and optical electronic absorption spectroscopy. A delayed onset of the charge-resonant electronic absorption signal of several aliphatic diamine (including TMEDA) radical cations in rigid matrix environments indicate a structure-dependent intramolecular charge delocalization. A recent RFS study showed that a 209 nm photon excites the TMEDA molecule to a 3p Rydberg state.
with a charge-localized ion core. Rapid internal conversion from 3p to 3s generates a multitude of conformational structures, including one where the nitrogen lone pair orbitals align to enable the charge delocalization between the two nitrogen atoms. Because the internal conversion populates multiple conformeric structures, including some that are close to that of the original ground state, as well as the charge-delocalized structure, the structural details of the charge delocalization reaction have remained hidden in these previous studies. In exploring the dependence of the charge transfer dynamics on the excitation energy we found that lower energy pump photons excite TMEDA directly to the 3s Rydberg state, which unmasked the structural motions that lead from the Franck-Condon region to the charge delocalized state.

The contour plot of the time-resolved Rydberg electron BE spectrum is shown in Figure 1a. The 239 nm (5.19 eV) pump pulse resonantly excites TMEDA to the 3s Rydberg state and the 404 nm (3.07 eV) probe pulse monitors the time-dependent dynamics by ionizing the Rydberg-excited molecules. In analogy to our previous studies of other tertiary amines and the recent RFS study on TMEDA, we assign both distinct peaks, at about 2.84 and 2.69 eV, to 3s Rydberg states associated with distinct molecular structures. We label the two peaks as 3s_h and 3s_l, where h and l denote the higher and lower BE, respectively. Figure 1b shows the energy-integrated intensities of the 3s_h (2.64-2.75 eV) and 3s_l (2.75-2.95 eV). Figure 1c plots their corresponding fractions. In the observed time window the total intensity of the 3s state does not decay. This compares to a relatively short life time (6.77 ps) of the 3s state when the molecule is excited with a higher energy 209 nm photon. The dependence of electronic state lifetimes on vibrational excitation has previously been documented. In N, N-dimethylisopropylamine the lifetime of the 3s Rydberg state decreases exponentially with the amount of vibrational energy. Assuming equal ionization cross-sections for the two states and
given careful calibration of the intensity sensitivity of the photoelectron spectrometer for electrons with different kinetic energies, the fractional intensity represents the populations of the different structural forms. It is apparent that the 239 nm photon populates the 3s\textsubscript{h} state directly but the flow of energy leads to populate the 3s\textsubscript{l} peak until an equilibrium is reached.

![Figure 1](image)

**Figure 1.** (a) The time-dependent Rydberg electron BE spectrum. The colors represent the signal intensities on a natural logarithmic scale and the color bar gives the scale range in arbitrary units. 3s\textsubscript{h} and 3s\textsubscript{l} represent the 3s component peaks with higher and lower BE, respectively. (b) The time-dependent signals of the two spectral features in arbitrary units (3s\textsubscript{h} in blue diamonds and 3s\textsubscript{l} in green squares). (c) The time-dependent intensity fractions of the 3s\textsubscript{h} and 3s\textsubscript{l} peaks. Solid lines in (b) and (c) represent the best fits of the experimental data using the Levenberg-Marquardt algorithm with a kinetics model of first order reactions and a two-component equilibrium. The values of the fit parameters are discussed in the text.

Assuming first order kinetics and adopting the formalism of a two-component system that is suddenly displaced from its equilibrium,\textsuperscript{12,28} the experimental data of the intensities and the fractional ratios can be fitted as shown by solid lines in Figure 1b and 1c. The forward and
backward time constants of the reaction from 3s_h to 3s_l were determined to be 1.19 (0.14) ps and 2.61 (0.31) ps, respectively. Values in the parentheses give the 3σ uncertainty of the fits. These time constants for the equilibrium are much slower than those measured in the experiment where the molecule was pumped with 209 nm,15 which are 490 (55) fs and 621 (56) fs for the forward and backward reactions, respectively. The slower equilibrium rates are likely due to the lower available vibrational energy in the longer pump wavelength experiment and are reminiscent of the longer electronic state lifetimes. Once the equilibrium is reached, the population ratios are 0.267 (0.013) and 0.733 (0.013) for the 3s_h and 3s_l peaks, respectively. At time zero, the displacement of the population ratio from the equilibrium value is 0.563 (0.031). In the prior experiments with 209 nm pump photons the equilibrium population ratios were 0.415 (0.027) and 0.585 (0.027) for the 3s_h and 3s_l peaks, respectively, and the population ratio displacement was 0.269 (0.070). The larger equilibrium population in the higher pump wavelength experiment indicates negative enthalpy and entropy changes for the reaction from 3s_h to 3s_l. Similar observations have been made for cyclic diamines.29

To explore the dynamical pathway that leads TMEDA from the Franck-Condon region to the equilibrium we honed in on the early time dynamics by increasing the number of delay time steps within the first 2 ps. At small delay times we discovered several distinct binding energy peaks in the time-resolved Rydberg electron BE spectrum, indicated by numbers 1 through 4 in Figure 2a. At time zero, the 3s_h peak arises first in position 1 while the 3s_l peak has negligible intensity at that time. As time passes, the 3s_h peak center migrates towards higher BE’s, reaching position 2 at 0.6 ps. It then moves back toward a lower BE, position 3, and becomes constant after about 1 ps. During this entire process, the 3s_l peak retains a constant BE. We
interpret this observation as reflecting structural dynamics amongst distinct conformeric structures, superimposed on the overall approach to the equilibrium distribution.

**Figure 2.** (a) The early part of the time-dependent Rydberg electron BE spectrum, with four distinct peak positions labeled by numbers 1 through 4, in the $3s_h$ and $3s_l$ regions. (b) The peak centers of the deconvoluted $3s$ peak with higher binding energy ($3s_h$, blue diamond and line) and lower binding energy ($3s_l$, green square and line). Numbers 1 to 4 indicate the same four positions as in part (a).
To obtain the center positions of the discrete peaks we fitted the spectra at each time point with one Lorentzian function in the time range of 0 to 0.23 ps and two Lorentzian components thereafter. This yields the time dependent peak center positions of the 3s\_h and 3s\_l peaks as shown in figure 2b. The solid lines in light blue and light green show the best fits of the equilibrium peak center positions of the 3s\_h and 3s\_l peaks, respectively, after they have settled to constant values. The peak positions are listed in Table 1.

To assign the observed spectroscopic features to molecular structures we calculated the BEs for the known minimum energy structures of the ground state and the ion state.\textsuperscript{15} TMEDA conformers are labeled with G or gauche, T or trans, and G' or gauche', meaning that the dihedral angle D(LP–N–C–C) or D(N–C–C–N) is in the range of 0° to 120°, 120° to 240°, and 240° to 360° or -120° to 0°, respectively. LP stands for the electron lone pair of the N atom. The folded GG'G structure is the global minimum in the ground state and is the one present in the molecular beam. In the cation, the three most stable conformers are TTT\textsuperscript{+}, GGG'\textsuperscript{+} and GG'G\textsuperscript{+}. The fully stretched TTT\textsuperscript{+} conformer was found to be the global minimum in the cationic ground state. Starting the optimization on the ion potential surface with the ground state global minimum GG'G conformer gave the GG'G\textsuperscript{+} structure. The charge-localized GG'T\textsuperscript{+} structure was obtained by optimizing the GG'G conformer with one nitrogen semi-planar as the starting structure on the ion potential surface.

For each of these cationic structures we calculated the BEs using the DFT-SIC method. Implicit in this approach is the assumption that the Rydberg electron has a negligible effect on the structure of the molecular ion core so that the cationic structures resemble those of the corresponding ion cores of the Rydberg excited molecules. Because nuclear motions are much slower than those of the electrons, at delay times close to zero the molecule should retain its
ground state structure. We therefore also calculated the BE of the GG'G structure in the Franck-Condon region. The calculated BEs and relative energies (REs) of the 3s Rydberg states are listed in Table 1.

**Table 1.** Experimental BE peak center positions, the calculated BEs and the relative energies of the 3s Rydberg states. The values in the parentheses show the last digits of the 1σ uncertainty.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experimental</th>
<th>Calculated</th>
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<tbody>
<tr>
<td></td>
<td>BE/eV</td>
<td>BE/eV</td>
</tr>
<tr>
<td>1</td>
<td>2.81 (1)</td>
<td>2.79</td>
</tr>
<tr>
<td>2</td>
<td>2.86 (1)</td>
<td>2.88</td>
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<td></td>
<td></td>
<td>2.88</td>
</tr>
<tr>
<td>3</td>
<td>2.83 (1)</td>
<td>2.85</td>
</tr>
<tr>
<td>4</td>
<td>2.70 (1)</td>
<td>2.71</td>
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</table>

The calculated BEs are in excellent agreement with the experimental observations for the given assignments. In the Franck-Condon region, the molecule retains the ground state structure GG'G, for which the calculated BE, 2.79 eV, matches quite well with the experimental value of 2.81(1) eV. Since the Frank-Condon structure is unstable and has a very high energy (0.85 eV) on the potential surface of the 3s Rydberg state, the TMEDA molecule evolves its structure to find a nearby minimum. Because of the negligible interaction of the electron lone pairs in the ground state structure, the optical excitation leads to a 3s Rydberg state with the charge center at one of the nitrogens, which becomes planar upon excitation. Optimization from the ground state structure GG'G on the ion surface with different initial conditions yields, as pointed out, the GG'G' and GGT' structures. The GG'G' conformer shows a through-space-interaction (TSI) and partial charge delocalization between the two nitrogens, while the GGT' conformer has the charge localized on one nitrogen atom. The calculated BEs of the GG'G* and GGT* structures are both 2.88 eV, which agrees well with the experimental value of 2.86(1) eV. The
continuously increasing BE from peak position 1 to 2 reveals the structural dynamics of the TMEDA ion core upon excitation to the Rydberg state. The structural change mainly involves the nitrogen bending motion and a minor internal rotation (D(LP–N–C–C) and D(N–C–C–N)). These motions are probably coupled and all contribute to the BE change. The GG'G' and GGT' structures are therefore both considered to contribute to the peak intensity at 2.86(1) eV.

The two most stable conformers GGG' and TTT' both have through-bond-interaction (TBI) and a complete charge delocalization between the two nitrogens. Reaching these structures from the Franck-Condon structure requires substantial internal rotation, i.e., large changes of the dihedral angles D(N–C–C–N) and the two D(LP–N–C–C). This means that the TMEDA molecule needs to sample the multi-dimensional potential surface until it finds the proper geometry where the two lone pairs have strong TBI and the charge can delocalize. The BEs calculated with the GGG' and TTT' structures are 2.85 eV and 2.71 eV respectively. Therefore, peak position 3 with 2.83(1) eV BE is assigned to 3s Rydberg state with the GGG' structure and peak position 4 with 2.70(1) eV BE is assigned to 3s with the TTT' structure. While initially, these two states are at non-equilibrium populations, they continue to convert into each other until an equilibrium is reached. Since the 3s_1 peak dominates the intensity at long delay times (Figure 1), the assignment is also consistent with the equilibrium composition where the TTT' structure has the lowest total energy (Table 1).

Based on these assignments, the structural motions associated with the CT comes into focus. Excitation from the ground state to the 3s Rydberg state initially places a positive charge on only one of the nitrogen atoms and creates a charge-localized state. But the FC geometry is not a favorable one, so that the molecule relaxes to lower its potential energy, resulting in a structural change that is observed as a movement of the BE towards the higher region. One of the
relaxed structures, GGG⁺, exhibits TSI and a delocalized charge character, while another, the GGT⁺ conformer, has a localized charge. The molecule has sufficient internal energy to continue to sample the potential surface so that it is able to find the geometries of GGG⁺⁺ and TTT⁺, which have TBI and completely delocalized charges. As the TTT⁺ conformer gains in population, the back reaction sets in, which, on a picosecond time scale, leads to a dynamic equilibrium that is dominated by GGG⁺⁺ and TTT⁺. The forward and backward time constants of the reaction from 3s_h to 3s_l are 1.19 (0.14) ps and 2.61 (0.31) ps, respectively.

The present study on TMEDA shows the capability of time-resolved RFS to probe the structural dynamics of molecules with large amount of vibrational energy. The large size of the 3s Rydberg orbital and the sensitivity of its BE on the molecular structure make RFS a powerful tool to probe structure-dependent interactions, such as CT reactions, in large molecules. The ability of the DFT-SIC method to accurately calculate the BEs is essential to positively identify the molecular structures from the observed spectroscopic features. While these computations can explain the major features of the spectra, the BEs can, at the present time, only be applied to sample select structures. The experimental RFS, however, have richer dynamics information as they cover the complete evolution of the molecular structure, including structures outside of the minima on the potential energy landscape. Future binding energy and trajectory calculations on the 3s Rydberg surface might resolve in even more clarity the structural changes that occur when the charge delocalizes in TMEDA.

Experimental Details

The photoelectron spectroscopy apparatus has been described previously. Photoelectrons were detected using microchannel plate detectors and their flight times were converted to kinetic energies. The binding energy of an electron in a Rydberg state was determined by subtracting the
kinetic energy from the probe photon energy. The laser system has been described. Briefly, the 239 nm pump pulse and 404 nm probe pulse were generated by an optical parametric amplifier (Coherent Opera SOLO) and BBO upconversion crystals, respectively, with the 808 nm fundamental pulses from a two-stage amplifier (Coherent Legend Elite Duo) at 5 kHz repetition rate. The laser beams were focused perpendicularly onto the molecular beam, which was generated by entraining TMEDA at -30 °C in a stream of helium carrier gas and expanding through a 100 μm nozzle and a 150 μm skimmer. The time zero of the laser pulse overlap was determined by monitoring the cross-correlation between the pulses using the molecular response of 1,4-dimethylpiperazine, giving a cross-correlation time of 97(2) fs FWHM.

The structures and relative energies of the ground state and ion state of TMEDA used to calculate the BEs in this work have been reported elsewhere. The BEs of the Rydberg states were calculated using the DFT-SIC method with the Perdew-Zunger self-interaction correction, carried out with the GPAW program in real space with a cubic simulation box of 25-Å side length and a uniform 0.15-Å grid. The Rydberg orbitals were calculated using the ground state DFT-SIC with the local density approximation (LDA) functional. The total energy of the Rydberg-excited state was calculated with the PBE functional and the Delta Self-Consistent Field method where one electron was removed from the highest occupied orbital (HOMO) and placed in the desired Rydberg orbital. The binding energy of the Rydberg excited state was then obtained by subtracting the total energy of the excited state energy from that of the ion. This approach has shown to give good results for both small molecules and large molecular clusters.

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