Time-Resolved Conformational Dynamics in Hydrocarbon Chains

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Internal rotation about carbon-carbon bonds allows *N*,*N*-dimethyl-2-butanamine (DM2BA) and *N*,*N*-dimethyl-3-hexanamine (DM3HA) to assume multiple conformeric structures. We explore the equilibrium composition and dynamics between such conformeric structures using Rydberg fingerprint spectroscopy. Time constants for conformeric interconversion of DM2BA (at 1.79 eV of internal energy) are 19 and 66 ps, and for DM3HA (1.78 eV) 23 and 41 ps. For the first time, a time-resolved and quantitative view of conformational dynamics of flexible hydrocarbon molecules at high temperatures is revealed.

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The potential energy landscapes of large molecules are complex and multidimensional, so that the rotation about single chemical bonds enables molecules to change their overall shape. This has profound consequences for the chemical dynamics of large molecules, and indeed defines the function of macromolecules and biopolymers [1–3]. Yet in spite of many advances in experimental methodology [4–7], the exploration of molecular folding events in real time remains difficult.

Large molecules under equilibrium conditions have many conformeric forms. Transformations between conformers are possible when the internal energy exceeds the barriers that separate the potential energy minima [8]. Most time-resolved spectroscopic techniques [9] are not applicable under such conditions because the hot, flexible molecules have highly congested vibrational spectra [10,11]. In light of these challenges new experimental approaches are needed to observe conformational dynamics in real time. We report here the first application of the recently developed time-resolved Rydberg fingerprint spectroscopy (RFS) method to observe the conformational dynamics of hot hydrocarbon chain molecules.

RFS exploits the fact that the binding energy of an electron in a Rydberg state, i.e., the energy with which a highly excited electron is bound to the positive ion core, is exquisitely sensitive to the geometric structure of the molecule [12–15]. The binding energy spectrum can therefore be used to fingerprint the size and shape of molecules. Even structural changes far from the positive charge have been found to affect the term value of the Rydberg states. Yet, RFS spectra were found to be remarkably insensitive toward thermal excitation, as they provide a purely electronic spectrum [16,17]. RFS can be implemented in a time-resolved pump-probe scheme, making it possible to observe the time evolution of molecular structures [18]. Time-resolved RFS is therefore uniquely suited to explore the time-dependent interconversion between conformeric forms of flexible molecules, internally excited to chemically significant energies.

We investigated two saturated hydrocarbons connected to tertiary amine groups: *N*,*N*-dimethyl-2-butanamine (DM2BA) and *N*,*N*-dimethyl-3-hexanamine (DM3HA). Internal rotation about C-C single bonds provides the aliphatic chains with a complex conformeric energy landscape. The amine groups support a positive charge about which the Rydberg electron orbits. The Rydberg-excited system thus consists of a positive ion core at the amine site and a diffuse Rydberg electron cloud. For the principal quantum number of our experiment, the Rydberg wave function has a dimension of 1–2 nm, thus completely encompassing the conformational structure of the molecule.

Experiments were conducted by seeding the sample in a helium carrier gas and entraining it in a molecular beam apparatus outfitted with a photoelectron spectrometer [19,20]. The molecules were excited and ionized by the sequential absorption of two photons having durations of 13 ps. A 207.9 nm photon excites the sample to the 3*p* Rydberg state, and the RFS spectrum, in terms of the electron‘s binding energy, is obtained upon ionization with a 415.8 nm photon (Fig. 1).

Previous work on the internal energy flow in tertiary amines [17] shows that excitation from the ground state to the 3*p* Rydberg state deposits 1.25 eV into vibrations. Rapid (<1 ps) internal conversion from 3*p* to 3*s* adds to the vibrational energy. Once in 3*s*, the total vibrational energy of DM2BA is 1.79 eV, while DM3HA has 1.78 eV. Intramolecular vibrational relaxation quickly distributes this energy, leaving DM2BA and DM3HA with effective temperatures of 950 and 810 K, respectively. This internal energy is sufficient to surmount the barriers to internal rotation, allowing the molecules to convert between conformeric structures.

Time- and energy-dependent RFS spectra of DM2BA are shown in Fig. 2. Plotted is the 3*s* signal intensity as a function of the electron‘s binding energy and delay time between laser pulses. The spectral line shape, projected for two time delays, has a time-dependent structure. Molecular vibrations do not contribute to the width of the spectral line [17]. Therefore, the line shape reflects a dispersion of molecular structures, and its time dependence reveals an evolution of the conformeric composition. The line shape

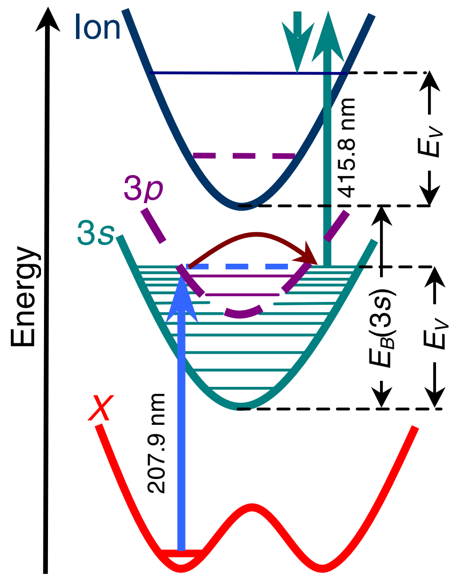

FIG. 1 (color online). Two-color excitation-ionization scheme: Excitation by a 207.9 nm photon excites the amine to the $3p$ Rydberg state, which rapidly decays to the lower $3s$ state. Ionization by a time-delayed 415.8 nm photon reveals the binding energy of the Rydberg electron E_B. The vibrational energy content E_V does not change during ionization.

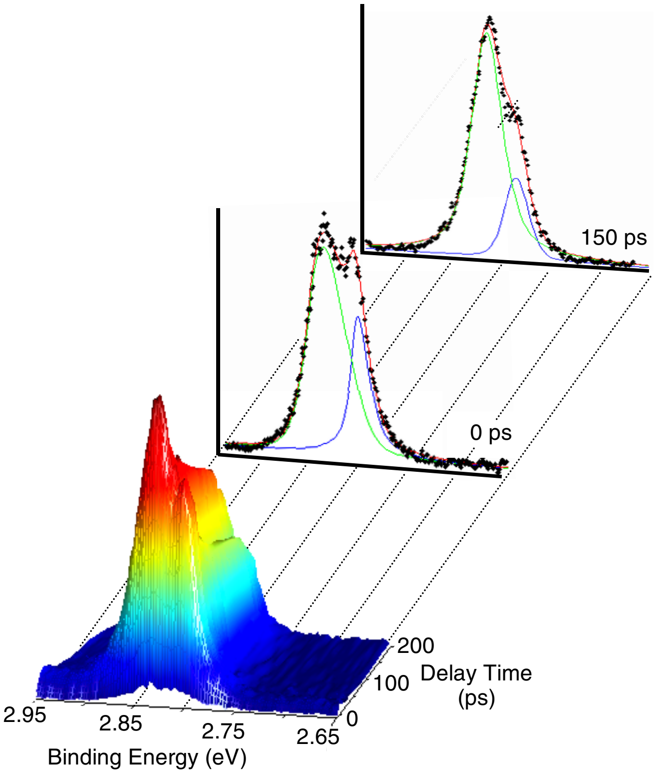

FIG. 2 (color online). Time- and energy-dependent RFS spectra of DM2BA. Only the region of the $3s$ Rydberg peak is shown. The back-projected spectra are individual slices taken at the indicated pump-probe delay times. The component peak curves in the individual spectra comprise the overall fit of the experimental data.

of the $3s$ peak for DM2BA is well fitted as a superposition of two peaks (Fig. 2) as a result of two conformeric forms dominating the landscape. The cross sections for ionization from $3s$ for different conformeric forms of the same molecule are expected to be similar, because the observed lines entail the complete Franck-Condon envelopes.

We calculate the fractional populations of the two dominant forms by comparing the areas of the substituent peaks. The time evolution of these fractional peak intensities, Fig. 3, reveals that starting from an initial population distribution the conformeric composition changes to a final equilibrium value on a time scale of tens of picoseconds.

Analysis of the changing conformeric composition follows that of fast chemical equilibria displaced by a sudden jump in experimental conditions [21]. There are two dominant conformeric forms, A and B, in equilibrium via opposing first order reactions:

$$A \underset{k_B}{\overset{k_A}{\rightleftarrows}} B.$$

With conformers A and B initially at equilibrium, the rapid change in temperature and conformeric energy landscape upon electronic excitation leads to a new equilibrium that is approached following an exponential time dependence, with a rate $k_A + k_B$. The time-dependent fractional population of conformer A is [22]

$$A(t) = A_e + x_e e^{-(k_A+k_B)^{-t}}.$$

Deconvolution of the observed time dependence from an instrument function, obtained in the experiment by observing the ultrafast transient $3p$ level, provides us with the fits in Fig. 4. We obtain the $t = 0$ populations $A_0 = A_e + x_e$ and $B_0 = 1 - (A_e + x_e)$, the final populations A_e and $B_e = 1 - A_e$, and the rate constants $k_A + k_B$. Since $B_e/A_e = k_A/k_B$, all kinetic parameters can be calculated (Table I).

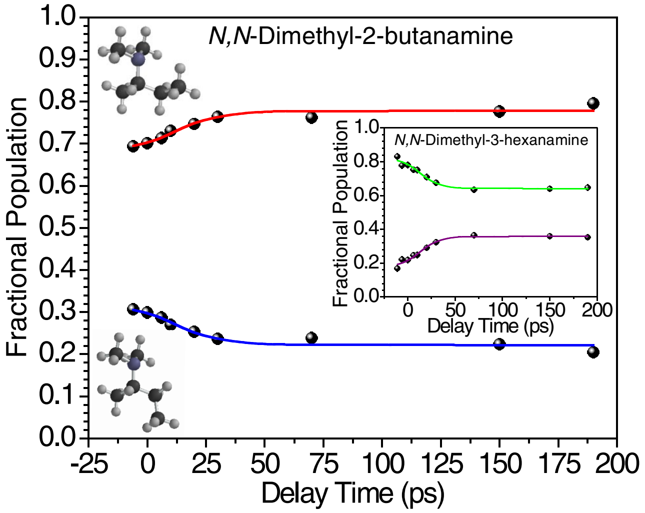

FIG. 3 (color online). Fractional population of the two conformeric forms of DM2BA and DM3HA (inset). The experimental data (dots) were fitted to a theoretical model assuming first order reactions between conformers and a convolution of the instrument function.

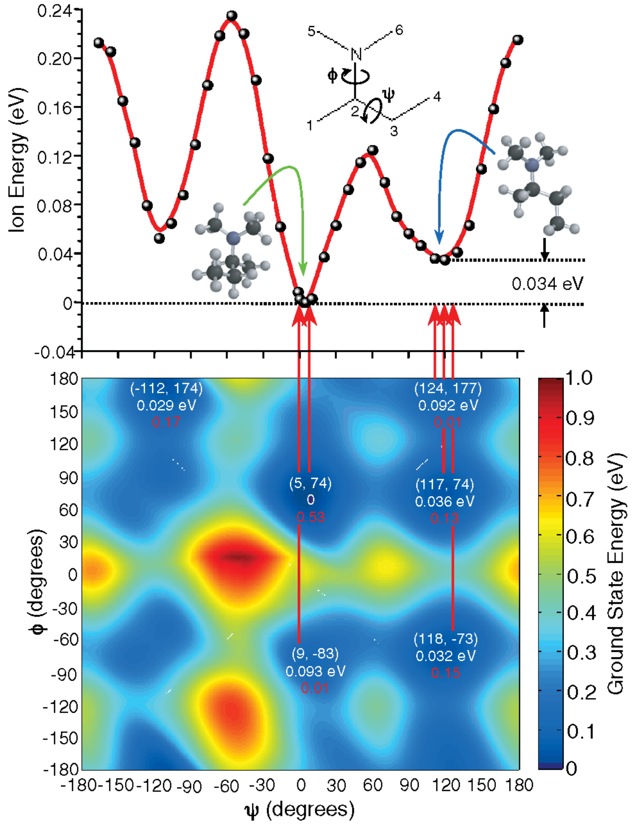

FIG. 4 (color). Bottom: Ground state potential energy of DM2BA as a function of the dihedral angles ψ and ϕ, identified in the inset above. Color bar energies are relative to the lowest energy structure (antibutane) at $(\psi, \phi) = (5°, 74°)$. The other, most relevant minima are labeled by their coordinates and energy above the global minimum. The populations at room temperature are given (red numbers). Top: The ion potential energy of DM2BA, calculated using DFT, features two minima. Transitions from the ground state surface to the excited state are indicated by arrows.

In DM2BA, the two conformeric forms are initially at populations of 0.67 and 0.33, respectively. As time passes, the conformers interconvert with time constants of 66 ps for the forward reaction $A \longrightarrow B$, and 19 ps for the back-reaction $B \longrightarrow A$, to reach an equilibrium composition of 0.78 and 0.22, respectively. Similarly, the conformers of DM3HA interconvert with time constants of 41 and 23 ps from a 0.85/0.15 to a 0.64/0.36 mix.

The identity of the DM2BA conformers is unmasked by calculating the ground state energy landscape and a one-dimensional calculation of the excited state. As tested by spot checks using density functional theory (DFT) at the B3LYP/6-31G(d) level, a molecular mechanics calculation provides a good potential energy landscape for the ground electronic state. For the Rydberg-excited molecules, higher-level calculations were needed. *Ab initio* calculations for such systems are difficult, but it is possible to calculate the energy of the corresponding ions. The energy of the Rydberg state differs from the ion energy by the binding energy of the electron, which is measured in the experiment. We therefore complement a DFT calculation of the ion at the B3LYP/6-31G(d) level with the experimental data to obtain relative well depths.

Figure 4, bottom surface, shows the ground state conformational energy landscape of DM2BA as a function of the internal rotation about the C-N (ϕ) and C-C (ψ) bonds. The calculation allowed the four free methyl rotors to assume the lowest energy structure. The zero of the ϕ rotation is where C5 eclipses Cl, while the zero of the ψ coordinate is where Cl and C4 are in antiposition (inset of Fig. 4).

The ground state surface has several distinct minima, with the lowest energy structure belonging to the $(\psi, \phi) = (5°, 74°)$ conformer. Five other minima are close enough in energy to be thermally populated at room temperature. Their coordinates, energies above the global minimum, and thermal populations are superimposed on the contour plot of Fig. 4. The inversion motion of the pyramidal amine group creates a second potential energy surface with symmetry-equivalent minima.

Excitation of the molecule to the Rydberg surface alters the energy landscape because the amine group becomes planar and the charge distribution changes. The planarity of the amine group increases the symmetry such that along the ϕ coordinate only two, symmetrically equivalent, minima remain. Since these minima are indistinguishable we focus on the one-dimensional ψ coordinate dependence of the ion core energy (Fig. 4, top). All other coordinates, including ϕ, are allowed to adjust for the minimum energy.

The two minima on the ground state surface at $(\psi, \phi) = (5°, 74°)$ and $(9°, -83°)$ map directly onto the excited state minimum at $\psi = 4°$ and one of the symmetry-equivalent wells at $\phi = 118°$ or $298°$. A vertical Franck-Condon transition from either of those ground state minima leads to Rydberg-excited structures in the $\psi = 4°$ well, as indicated by vertical arrows in Fig. 4. Similarly, the populations in the three minima with $\psi = 124°$, $117°$, and $118°$ map onto the excited state minimum at $\psi = 112°$. The ground state minimum at $(\psi, \phi) = (-112°, 174°)$ becomes sterically unfavorable upon excitation and becomes difficult to excite. Even if it were, the resulting

TABLE I. Folding or unfolding kinetic parameters for investigated hydrocarbon chains.

	Initial population ($A_e + x_e$)	Final population (A_e)	k_A/k_B	Observed $k_A + k_B$	k_A (τ)	k_B (τ)
DM2BA (950 K)	0.67	0.78	0.28	6.8×10^{10} s^{-1}	1.5×10^{10} s^{-1} (66 ps)	5.3×10^{10} s^{-1} (19 ps)
DM3HA (810 K)	0.85	0.64	0.56	6.7×10^{10} s^{-1}	2.4×10^{10} s^{-1} (41 ps)	4.3×10^{10} s^{-1} (23 ps)

conformer would decay rapidly along a repulsive coordinate. Consequently, of all the minima in the ground state, only two distinguishable structures remain, namely, the ones with $\psi = 4°$ and $112°$. This is consistent with our observation of two distinct peaks in the RFS spectra.

To assign the Rydberg peaks to particular conformational structures we consider the peak intensities. Before conformational dynamics ensues in the excited state, the populations of the two conformers in the Rydberg state are given by their respective ground state population. Given the energetics of the different ground state minima, we can calculate these populations for a room temperature sample. They are 0.54 for the lower energy structure at $\psi = 4°$ and 0.29 for the $\psi = 112°$ conformer. The calculated fractional populations at $t = 0$ are expected to be 0.65 and 0.35 for the $\psi = 4°$ and $\psi = 112°$ conformers, respectively. This is in excellent agreement with our experimental observation, where at $t = 0$ we find 67% of conformer A and 33% of conformer B. Therefore we identify conformer A of DM2BA, $E_B = 2.835$ eV, to have $\psi = 4°$ (antibutane), while conformer B, $E_B = 2.801$ eV, has $\psi = 112°$ (*gauche* butane).

The observed transformation between conformeric structures results from the rapid increase in the temperature of the molecule upon electronic excitation and from the change in the conformeric energy landscape. According to the calculations for the ions, conformer A has an energy that is 0.034 eV below that of conformer B. From the RFS spectra, we know that the binding energy for conformer A is 0.034 eV larger than that of conformer B. Therefore, in the Rydberg state, conformer A has a minimum energy that is 0.068 eV below conformer B. At previously estimated temperature of 950 K [17], this leads to a final ($t \rightarrow \infty$) distribution of 70% and 30% for conformers A and B, respectively. This is in good agreement with the observed final populations of 78% and 22%, respectively, further confirming the first order opposing reaction kinetic model and the assignment of conformeric structures to Rydberg peaks. Thus, all the structural and dynamic aspects of the conformerization of DM2BA are fully determined.

Ionization from a Rydberg state is unique in that it is purely electronic and uncoupled from vibrational transitions. Photoionization spectra from Rydberg levels are therefore not affected by the thermal congestion associated with molecules at high temperatures, providing purely electronic spectra that are sensitive to the molecular structure. This property allows us to investigate the time-resolved conformational dynamics of flexible molecules at chemically significant energies. The creation of a charge center by a fast laser pulse provides a convenient method to induce a change in the conformational energy landscape, to which the molecule responds by adjusting its equilibrium distribution. Calculations of the ground state energy surface of DM2BA are in excellent agreement with our observed distribution at $t = 0$, providing a reliable method to identify its conformers. In the excited state, the computational results for the ion can be coupled with the measured electron binding energy, and compared against the experimentally determined kinetic equilibrium parameters. In DM2BA at 950 K, the tightly folded gauche butane reacts with a 19 ps time constant to the less folded antibutane structure, while the backreaction proceeds on a 66 ps time scale.

Our study provides a time-resolved and quantitative view of conformational dynamics of isolated, flexible molecules at high temperatures. The methodology should be applicable to a wide range of molecular sizes, as trade offs between spectral and temporal resolution can be selected to meet the requirements of individual systems. Selection of Rydberg states with different principal quantum numbers offers additional flexibility to accommodate larger systems, possibly even biopolymers.

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