Energy Flow and Fragmentation Dynamics of *N*,*N*-Dimethylisopropylamine

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The energy flow and fragmentation dynamics of *N*,*N*-dimethylisopropylamine (DMIPA) upon excitation to the 3p Rydberg states has been investigated with use of time-resolved photoelectron and mass spectrometry. The 3p states are short-lived, with a lifetime of 701 ± 45 fs. From the time dependence of the photoelectron spectra, we infer that the primary reaction channel leads to the 3s level, which itself decays to the ground state with a decay time of 87.9 ± 10.2 ps. The mass spectrum reveals fragmentation with cleavage at the α C−C bond, indicating that the energy deposited in vibrations during the internal conversion from 3p to 3s exceeds the bond energy. A thorough examination of the binding energies and temporal dynamics of the Rydberg states, as well as a comparison to the related fragmentation of *N*,*N*-dimethyl-2-butanamine (DM2BA), suggests that the fragments are formed on the ion surfaces, i.e., after ionization and on a time scale much slower than the fluorescence decay from 3s to the ground state.

Introduction

The photochemistry of tertiary amines upon electronic excitation provides an important study of the interplay between nonradiative relaxation pathways between high-lying electronic states and the cleavage of covalent bonds. Motivated by such fundamental considerations, as well as by the role that amines play as building blocks of biopolymers such as proteins and nucleotide bases, a significant amount of effort has been expended on understanding the energy flow upon excitation of their excited electronic states.[1−4] Since the 1930s, it has been known that all of ammonia's electronic states are of Rydberg type, with the lowest excited state being the 3s Rydberg state.[5,6] The close relationship of the absorption spectra of substituted amines to that of ammonia led to the conclusion that the first excited states of those species also were the 3s Rydberg states, with the charge centers of the ion core located on the nitrogen atom.[7] Even so, it was recently suggested that in their 3s Rydberg states the simple amines, such as methylamine, may have ion cores with the positive charge delocalized over both the nitrogen and the neighboring carbon atoms.[8]

Tertiary amines exhibit, when excited to the low-*n* Rydberg states, very fast dynamics that reveals itself in broad absorption features.[9] As the mass spectra of tertiary amines often prominently feature the fragments that result from cleavage of the α bond, it is an intriguing question if the ultrafast relaxation dynamics manifest in the absorption spectra is, in fact, related to the bond dissociation. Sølling et al. recently used femtosecond time-resolved mass spectrometry to determine the reactive pathways of 10 aliphatic amines, including *N*,*N*-dimethylisopropylamine (DMIPA) and *N*,*N*-dimethyl-2-butanamine (DM2BA).[10] They interpreted the mass spectra by invoking a dissociation on the Rydberg surface after a fast internal conversion. In their analysis, then, the fragments are born on a Rydberg surface, and ionized by the subsequent probe laser pulse.

In our recent work we have shown that the binding energies of Rydberg states provide sensitive fingerprints of molecular structure and shape. The sensitivity toward molecular shape was demonstrated on a set of isomeric molecules. Even for closely related molecules, the Rydberg spectra yielded characteristic structural fingerprints that are useful for identification of each isomer.[11,12] Additional studies demonstrated that this Rydberg fingerprint spectroscopy (RFS) is sensitive to the charge distributions in a group of isomeric fluorophenols, and the global molecular structure for a group of aliphatic diamines.[13] Finally, we recently showed that RFS can be used to identify the charge center of a bifunctional molecule.[14]

For the present work on the pathway of energy relaxation and the fragmentation dynamics of tertiary amines, we reasoned that the structural fingerprint aspect of the Rydberg spectra could provide the most definitive tool to determine the surface on which the amines dissociate. As long as the parent molecule is still intact, one will observe the Rydberg level with a binding energy characteristic of the parent ion. As soon as the fragmentation occurs, the Rydberg spectrum will change to accommodate the newly formed molecular structure. Thus, a measurement of the time-dependent Rydberg spectra should provide for a detailed view of both the internal relaxation dynamics as well as the molecular fragmentation.

The experiment is conducted by using the scheme shown in Figure 1. An ultrashort laser pulse at 208.5 nm (fourth harmonic, (4ω)) excites the molecule initially to the 3p level. A nonradiative relaxation process brings the molecule to a lower electronic surface, depositing a large amount of energy into the vibrational manifold. A probe laser pulse (second harmonic, 2ω) is used to ionize the molecule at a variable delay time after the pump laser. We observe both the mass and the photoelectron spectra. The latter provides a spectrum of the binding energies, E_B, of the Rydberg states. Since the potential energy surfaces

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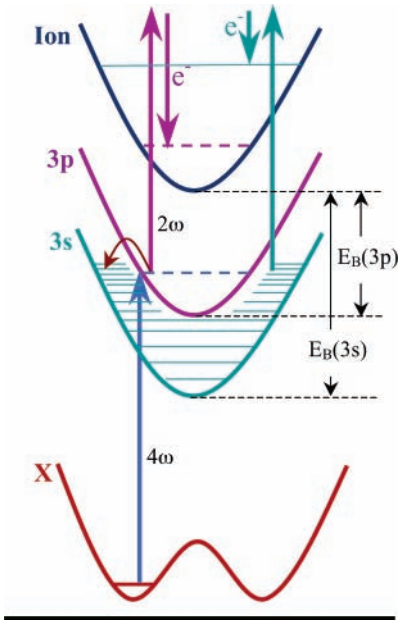


Figure 1. The employed excitation and photoionization scheme: A laser pulse (4ω) excites the tertiary amines to the 3p Rydberg states, which rapidly decay into the lower lying 3s state. Ionization by the time-delayed probe pulse (2ω) produces either high-energy electrons, if the ionization is from the 3p state, or low-energy electrons, if the ionization proceeds from the 3s state. E_B represents the binding energy of the electron in the respective states.

of the Rydberg levels and the ion state are close to identical,[15] the photoelectron spectra feature narrow peaks even when a large amount of energy is deposited into vibrational degrees of freedom.

Experiments were conducted primarily on *N*,*N*-dimethylisopropylamine, DMIPA. However, as is easily seen, other tertiary dimethylamines can provide the same fragments as the dissociation of DMIPA. As we will show, the time-resolved Rydberg fingerprint spectra, as well as the Rydberg fingerprint spectra of the fragmentation of other compounds, provide a definitive understanding of the energy flow and fragmentation dynamics of the tertiary amines.

Experimental Section

The photochemistry experiments described in this paper are conducted by seeding the tertiary amines in helium and expanding the sample in a molecular beam. Details of this apparatus, as well as the ultrafast laser system used to generate the short laser pulses, have been described previously.[16,17] Briefly, tunable femtosecond pulses between 780 and 840 nm are generated in a Ti:Sapphire oscillator laser that produces pulses with a 100 fs duration. The oscillator output is amplified to 5 μJ per pulse by a regenerative amplifier operating at a 50 kHz repetition rate. The fourth and second harmonics are generated with use of BBO crystals, providing 208.5 and 417 nm pulses that are used as the pump and probe pulses, respectively.

The molecular beam intersects the laser beam, which is focused to an intensity of 2×10^{12} W/cm^2 at the interaction region. Electrons are detected by a microchannel plate detector after traversing a field free drift tube. The spectral resolution of the electron spectrometer is better than 10 meV, and limited in the present experiments only by the time-bandwidth product of the laser pulses.

For detection of ions, acceleration voltages are applied to the interaction region, so as to direct the ions toward a second microchannel plate detector. The signal from both MCP's is amplified and analyzed by using fast timing electronics.

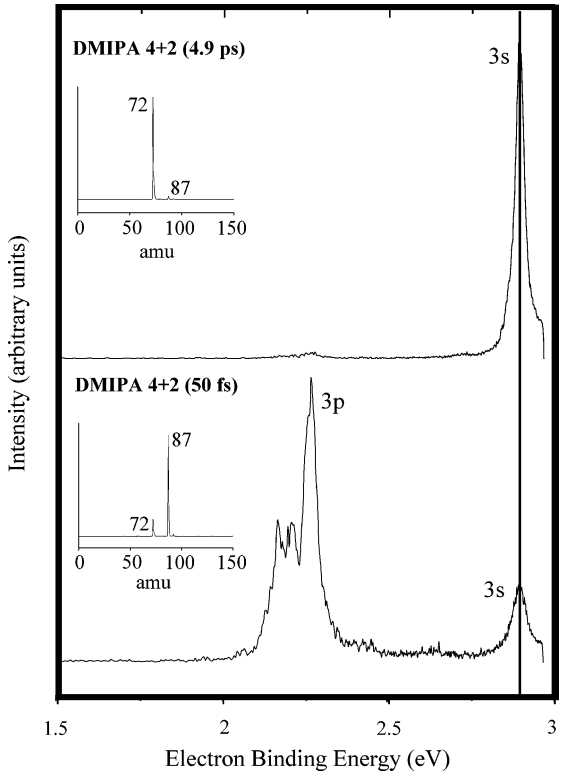


Figure 2. Photoelectron spectra and mass spectra (insets) of DMIPA, immediately after the excitation and after a delay time of 4.9 ps. The mass spectra show the parent mass 87 u, or the fragment with mass 72 u, while the photoelectron spectra reveal that the ionization is out of the 3p and the 3s state, respectively.

To minimize clustering, which is known to easily occur for amines,[18,19] all compounds were seeded in the helium carrier gas at a temperature of approximately −60 °C. DMIPA was purchased from Aldrich and used without further purification. *N*,*N*-dimethyl-2-butanamine (DM2BA) was synthesized from 2-butylamine in an Eschweiler−Clarke reaction.[20]

Results and Discussion

The photoelectron and mass spectra of DMIPA, taken immediately after photoexcitation (bottom panel) and after 4.9 ps (top panel), are shown in Figure 2. From the mass spectra we conclude that the parent ion, at mass 87 u, breaks apart predominantly by cleaving the α C−C bond, generating a fragment of mass 72 u. This fragmentation implies a loss of a methyl group from the isopropyl moiety, as was demonstrated in previous work by Sølling et al.[10] The photoelectron spectra show features belonging to the set of 3p states, as well as the 3s state. For short pump−probe delay times (bottom panel), most of the signal stems from ionization of the parent neutral in a 3p state, while at longer delays (top panel) the ionization proceeds almost exclusively out of 3s. The combination of the photoelectron and mass spectra shows that, at longer delay times, the generation of fragment ions is correlated with the ionization out of the 3s state. The spectra at short delay times suggest that ionization out of the 3p state leads to the parent ions.

More detailed information is obtained by observing the photoelectron and the mass spectra as a function of pump−probe delay time. Figure 3 shows the time dependencies of the mass spectra (bottom panels) and the photoelectron spectra (top panels) on the delay time, for short time delays (left panels)

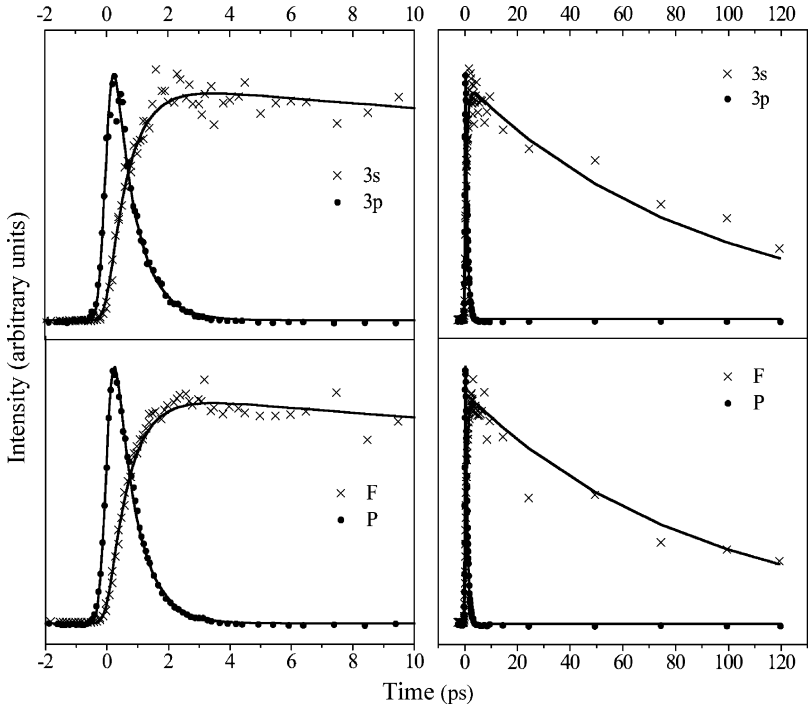


Figure 3. Time dependencies of the photoelectron signals (top panels) and ion currents (bottom panels) for short time delays (left panels) and long time delays (right panels). Parent and fragment ions are denoted by circles (P) and crosses (F), respectively.

TABLE 1: Time Constants Obtained in a Global Fit of All Time-Dependent Data, Together with Uncertainties (3σ)

parameter	time constant	uncertainty, 3σ
decay of 3p, rise of 3s, decay of parent, rise of fragment	701 fs	45 fs
decay of the 3s state	87.9 ps	10.2 ps

and longer time delays (right panels). An inspection of the data suggests that the temporal characteristics of the mass and the photoelectron spectra are identical. For this reason we modeled the data by assuming that electronic relaxation out of 3p directly populates the 3s level, which by itself decays on a slower time scale. There are thus only two time constants: one describing the decay of 3p and the simultaneous rise of 3s, and one for the slower decay of 3s. In addition we postulate that the parent ion signal has the same temporal profile as the 3p signal, and that the α-cleaved fragment behaves like 3s. With this model we implemented the Gauss−Newton method that utilizes an identity-weighting matrix to perform a least-squares fit optimization of all available data. Together with the two time constants, scaling factors and time-zero positions were determined. The fits derived from the simple model, shown in Figure 3, represent the observed data very well, and thereby justify our assumptions. The time constants for decay and rise times are listed in Table 1, with uncertainties reflecting 3σ intervals. It is seen that both the parent ion signal and the photoelectron signal of the 3p state decay with a time constant of 701 ± 45 fs. The rise of 3s, as well as the signal of the α-cleaved fragment, is identical. Finally, both the fragment ion and the 3s signal show a decay with a lifetime of 87.9 ± 10.2 ps.

Previous photophysical studies on trimethylamine, triethylamine, and tri-*n*-propylamine established that tertiary amines decay by fluorescence,[21] with a very high quantum yield.[22,23] Thus, the 87.9 ± 10.2 ps decay time that we observe in the 3s photoelectron peak and the mass spectrum of the fragment must be due to fluorescence. Indeed, we observe off-resonance multiphoton ionization signals that can be attributed to ionization by 3 and 4 photons of the second harmonic, respectively, which

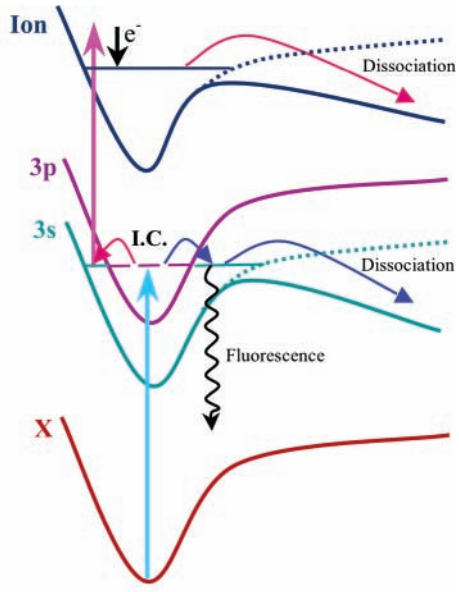


Figure 4. Excitation and fragmentation scheme of tertiary amines upon excitation to the 3p level. Rapid internal conversion to the 3s state deposits a large amount of energy into vibrations, sufficient for bond cleavage. Depending on how the dissociation competes with the parallel fluorescence, the dissociation could occur on the Rydberg surface, or after the ionization on the ion surface.

increase with delay time. This signal is consistent with the recovery of ground-state molecules formed by fluorescence from the 3s state.

The mass spectra by themselves can be interpreted as follows (Figure 4). The molecule is excited to 3p, which decays on a 701 ± 45 fs time scale to 3s. Ionization out of 3p leads to ions with very little internal energy, insufficient for cleavage of the α bond. As a result, the parent ions are observed with the same temporal profiles as the photoelectron 3p signal. The appearance of the fragment ions can be explained in two ways. First, it is

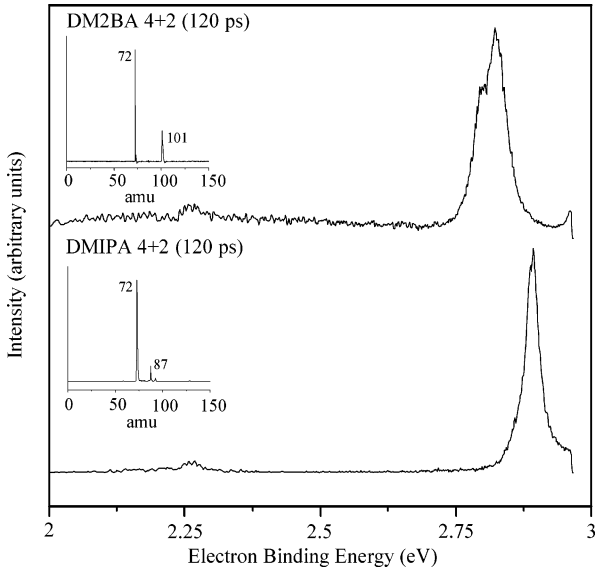


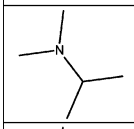
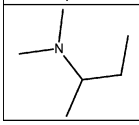
Figure 5. Rydberg fingerprint spectra and mass spectra (insets) of DMIPA and DM2BA, respectively, taken with delay times of 120 ps each. While the mass spectra show dissociation to the same fragment ions, the Rydberg spectra reveal that at the time of ionization the molecules have not yet fragmented.

possible that the molecule dissociates on the 3s surface, by virtue of the large amount of vibrational energy obtained during the internal conversion from 3p. In this scheme, which was espoused in previous work,[10] the fragments are born in the 3s Rydberg state, and ionized by the probe pulse. Naturally, this scheme leads to the observation of fragment ions. In a second scheme, the molecule acquires sufficient energy in the internal conversion to dissociate, but the time scale of dissociation is much longer than the fluorescence lifetime. The ionization by the probe photon leaves the vibrational energy content of the molecule constant, so that the parent ion that is initially formed has sufficient energy to fragment. As the molecule is accelerated by the ion optics toward the mass spectrometer, a process that is on a time scale of many nanoseconds, it may break apart, thus resulting in fragment peaks. The two schemes are equally valid interpretations of the mass spectra. We emphasize that mass spectrometry alone is not able to distinguish between the ionization pathways.

To determine which of the two fragmentation schemes is followed by DMIPA, we invoke the fingerprint spectral characteristics of the Rydberg states in two specific ways. First, we note that as the molecule dissociates on the 3s Rydberg surface, the binding energy of the Rydberg electron should change. As a result, the 3s Rydberg peak should shift in the photoelectron spectrum or, if the difference of the binding energies is very large, the initial peak should decay and a new 3s peak should grow as the molecule dissociates. No such manifestation of dissociation on the Rydberg surface was observed. For example, looking again at the spectra of Figure 2, we see that the 3s Rydberg peak stays at exactly the same energy. Thus, the data support only the second of the ionization/dissociation schemes, namely the dissociation on the ion surface.

It is conceivable that the binding energies of the Rydberg electrons associated with the parent and the fragment molecules just happen to coincide. On the basis of our previous experience with the Rydberg fingerprint method,[13] this is a very unlikely scenario. Nevertheless, independent confirmation would be desirable. Figure 5 shows a comparison of the mass and photoelectron spectra of DMIPA with those of *N*,*N*-dimethyl-2-butanamine, DM2BA. Both of these molecules feature two methyl groups as well as an aliphatic chain on the amine. The butylamine could lose either a methyl or an ethyl group; experimentally, only the latter one is observed in a reasonable yield. Thus, both the DMIPA and the DM2BA generate the very same fragment molecule, observed in the mass spectrum at mass 72.

TABLE 2: The Binding Energies (BE), Principal Quantum Numbers (*n*), and Quantum Defects (QD) of the Molecules Studied

Molecule	BE	n	QD
	2.27	3	0.55
	2.88	3	0.83
	2.26	3	0.54
	2.80	3	0.80

At this point the Rydberg fingerprint analysis makes a very clear distinction between the two fragmentation pathways. If the molecules were to dissociate on the Rydberg surface, ionization by the probe laser pulses would ionize the same fragment molecules, which should be observed as identical Rydberg peaks. On the other hand, if ionization precedes the fragmentation, then the ionization by the probe laser pulses would ionize the respective parent molecules, leading to distinctly different Rydberg peaks. As is shown in Figure 5, the Rydberg spectra obtained for the two molecules are clearly distinct. Thus, we have a second and independent evidence that the fragmentation occurs on the ion surface and not the Rydberg surface.

From the observed binding energies, we can determine the quantum defects associated with the respective Rydberg states.[13] Table 2 summarizes the values for the two molecules and the different Rydberg states. The quantum defects bear out our previous observation that they are sensitive to the molecular structure even though the two molecules feature the same chemical arrangements and bonds in the immediate vicinity of the nitrogen atoms.

Conclusions

Our study unambiguously identifies the fragmentation pathways of the tertiary *N*,*N*-dimethylisopropylamine when excited to the low-*n* Rydberg manifold. We observe an ultrafast internal conversion from 3p to 3s, proceeding on a time scale of 701 ± 45 fs. This relaxation process deposits a large amount of energy (1.4 eV) into vibrational coordinates, sufficient to break the weak α C−C bond. However, this bond cleavage cannot compete with the fluorescence decay of the molecule, which proceeds on a 87.9 ± 10.2 ps time scale. As a result, the molecules decay to the ground state before they can react on the Rydberg surface. While one can surmise that the molecules will then fragment on the ground electronic surface, such a process is outside the scope of our experiment. When the molecule is ionized by a time-delayed probe pulse, one observes fragmentation if and when ionization is out of the 3s state. That is, if the time delay is small, and the molecule is captured while still in the 3p state, the ionization leads to stable parent ions that are observed in the mass spectrum. If the time delay is larger than the electronic relaxation time, then ionization takes place from the 3s state. In that case the molecule has already acquired the vibrational energy necessary to dissociate, and on the slow time scale of mass spectrometry, one observes the fragment ions only.

Our study points out the perils of exploring molecular fragmentation dynamics using time-resolved mass spectrometry only. The mass spectra by themselves do not have sufficient information content to determine unambiguously on which surface a dissociation proceeds. As we have shown here, the combination of mass spectrometry and photoelectron spectrometry is able to clarify such questions by unambiguously identifying the specific surface from which ionization takes place. In the case of Rydberg states, as is the case in the present work, the photoelectron spectra are particularly informative as the sharp peaks of the Rydberg fingerprint spectroscopy allow highly specific identification of the ionizing molecule. Moreover, the fact that the Rydberg peaks are insensitive to even large amounts of vibrational excitation make the spectra easily assignable.

In the previous work by Sølling et al.,[10] time-resolved mass spectra were interpreted based on the assumption that fragmentation occurs on the Rydberg surface. While this interpretation is not consistent with our observations, we point out that the excitation scheme used in the previous study prepares Rydberg states with much higher quantum numbers. While it is possible that rapid internal conversion brings the molecules down to the 3p and 3s states that we probed, it is also possible that other photochemical processes are at play at the higher energies. It thus would appear interesting and important to explore the photochemistry of the tertiary amines using the higher excitation energies coupled with Rydberg fingerprint spectroscopy as we have done here.

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