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Excited-State Ions in Femtosecond Time-Resolved Mass Spectrometry: An Investigation of Highly Excited Chloroamines

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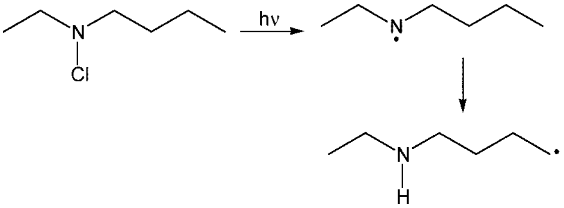
We have investigated the processes induced by femtosecond laser pulses in chloroamines, with a focus on the generation and observation of a highly reactive radical and on the involvement and general importance of excited-state ions in time-resolved mass spectrometry investigations of gaseous molecules. We have found that 280 nm femtosecond pulses lead to an ultrafast breakage of the N−Cl bond on the repulsive S_1 surface, and that resulting radical is long-lived. When exposing the molecule to 420 nm photons a multiphoton ionization takes place to generate ions; these ions can then be excited with a 280 nm photon. The evidence is unambiguous since we observe a distinct temporal evolution of the ion current with no photoelectrons to match. We suggest that the involvement of excited-state ions is a general phenomenon in time-resolved photoionization studies.

1. Introduction

The prerequisite for ultrafast bond breakage is the immediate activation of a reactive degree of freedom such as a bond stretching motion. There have already been a number of studies proposing excitation to repulsive surfaces resulting in immediate bond breakage,[1−3] a process that leads to the ultrafast formation of highly reactive radicals. The dynamics of the reactions of organic radicals remain largely unexplored with very few examples unequivocally being associated with radicals.[4] The principal reason for the ambiguity pertaining to studies of organic radicals is the methods used in studying gaseous molecules with femtosecond-resolved pump−probe experiments; usually an ionizing probe is employed and the energy transfer in the ionization process can cause fragmentation. Thus, it can be difficult to distinguish the ions that are formed by direct ionization from those that, misleadingly, are formed as a consequence of fragmentation of a larger ion. We have previously shown that ion decomposition plays a key role in the interpretation of femtosecond resolved dynamics in Rydberg excited amines and valence excited ketones.[5,6] It is, however, an open question how the actual decomposition is induced: does the laser induce the formation of an actual excited-state ion or is it rather a matter of the formation of a vibrationally hot ion in the electronic ground-state? Excited state ions have been studied extensively by Johnson with a method that was referred to as photoinduced Rydberg ionization (PIRI) spectroscopy,[7] and it was possible to address their isolated properties in a series of studies.[8,9]

Recently, we have conducted a study on aliphatic *N*-chloroamines to show that they are potential candidates for the formation of an organic radical that can further take part in the transfer of a hydrogen atom:[3] We showed that the lowest lying excited-state is, indeed, a repulsive valence state and that the subsequent states are bound Rydberg-states. Moreover, we found that the ionization energies of the chloroamines lie below the energy of two pump photons produced from a standard femtosecond laser system. Thus, the chloroamine system provides an exciting venue for the present exploration, in the sense that it is both possible to form a highly reactive organic radical and, if the oscillator strength related to the repulsive valence state is too low, pumping will result in an ion that will then become excited upon interaction with the probe. In the present paper we report our findings that shed light on the signal signature that results when excited-state ions are involved in femtosecond time-resolved mass spectrometry experiments.



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2. Experimental Section

The experimental setup in Copenhagen consists of a Ti: sapphire laser system from Spectra-Physics (Tsunami oscillator, Spitfire Pro amplifier), which delivers 130 fs, 1 mJ pulses at 1 kHz. The regenerative amplifier is tuneable from 760 − 860 nm but in this study the amplifier was operated with a fixed wavelength of 840 nm. The fundamental output of the laser was frequency doubled and tripled with two successive BBO crystals (0.5 mm, types I and II). The third harmonic (3ω) pulse (4.4 eV) was passed onto an automated delay stage and merged with the second harmonic (2ω) pulse (2.9 eV) before entering the sample chamber. The two pulses were overlapped on a molecular beam that was generated by expansion of the *N*-chloro-*N*-ethylbutylamine vapor (23 °C) seeded in He at 1.1 bar. *N*-Chloro-*N*-ethylbutylamine was synthesized analogously to the procedure described by Neale et al.[10] and the purity was verified by ^{1}H- and ^{13}C NMR spectroscopy and mass spectrometry. The beam was skimmed before entering a differentially pumped chamber. The typical energies used for the 2ω and 3ω

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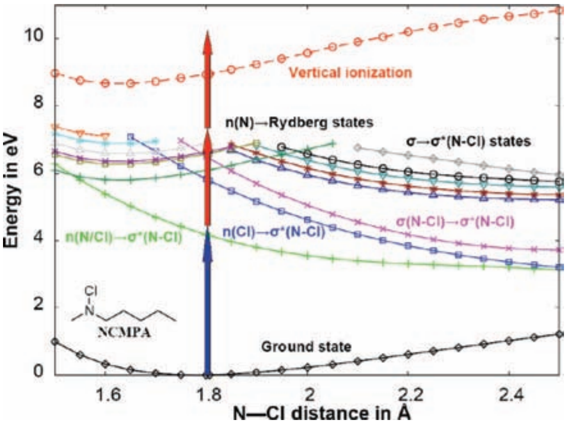

Figure 1. Potential energy surfaces along the N−Cl stretching motion in *N*-chloro-*N*-methylpentylamine.

pulses were ~100 μJ and ~20 μJ, respectively. The maximum intensity after focusing with 25 cm achromatic lens was estimated to be 3×10^{13} W/cm^2. These intensities are apparently not high enough to give rise to any significant ponderomotive potentials as no significant distortion was observed in the photoelectron spectra. Both photoelectrons and ions were detected using multichannel plate detectors, and the time-of-flight spectra were acquired by a multiscaler card (FastComTec) at different delays between pump and probe. The resulting transients were fitted to a kinetic model and the instrument function was included as described by Zewail.[11,12] We have verified that time-zero of the parent transient is the same as the time-zero that results from an in situ measurement with xenon. The full-width-half-maximum of the pulses was determined to be ~400 fs from the parent ion of a calibration compound (acetone) and xenon transients.

3. Results and Discussion

To fully understand the processes involved when *N*-chloro-*N*-ethylbutylamine is exposed to 280 and 420 nm femtosecond laser pulses it was necessary to employ a combination of quantum mechanical calculations, time-resolved mass spectrometry and photoelectron spectroscopy.

Computational Results. In our previous computational study of aliphatic chloroamines we addressed the nature of the vertical excitations and the potential energy surfaces along the N−Cl bond stretching motion at the TD-B3LYP/6-31+G(2df)//B3LYP/6-31G(d) level.[3] The ionization energies of the neutral parent and fragment species were calculated at the QCISD(T)/6-31G(d)//B3LYP/6-31G(d) level. The results for the excited states of the previously studied *N*-chloro-*N*-methylpentylamine model compound that are relevant to the interpretation of the experimental data are shown in Figure 1 and are discussed in the following.

The two lowest-lying excited states of *N*-Chloro-*N*-ethylbutylamine are repulsive along the N−Cl stretching coordinate. The electronic character is n(N) → σ*(N−Cl) in the case of S_1 whereas it is n(Cl)→ σ*(N−Cl) for S_2. The vertical transitions to these two states require 4.1 and 5.8 eV, respectively. This means that S_1 can be populated with a single 3ω photon. We note that the oscillator strength of the transition from S_0 to both S_1 and S_2 is low. The higher-lying states are bound along the N−Cl stretching coordinate; they are n(N) → Rydberg in nature. The Rydberg manifold can be reached with two 3ω photons (8.8 eV) or three 2ω photons for the higher-lying Rydberg states. However, in both cases a substantial amount of the excitations will lead to ionization since the ionization energy is 8.6 eV, less than the multiphoton energy. Nevertheless, the photon energies of both the 3 × 2ω and the 2 × 3ω combinations are very close to the ionization threshold, so that it is possible that either of these combinations will lead to the formation of Rydberg-excited species.

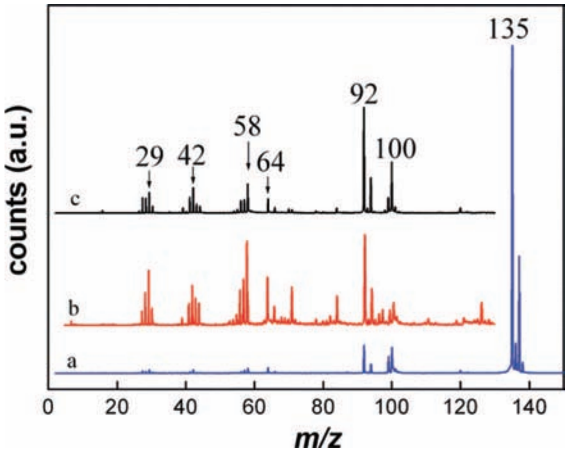

Figure 2. Mass spectra of *N*-chloro-*N*-ethylbutylamine obtained by (a) 2ω ionization and a source pressure of 3×10^{-6} mbar, (b) 3ω ionization and a source pressure of 2×10^{-7} mbar, and (c) 3ω ionization and a source pressure of 3×10^{-6} mbar. The spectra are normalized to the parent ion signal of part a and displaced for clarity.

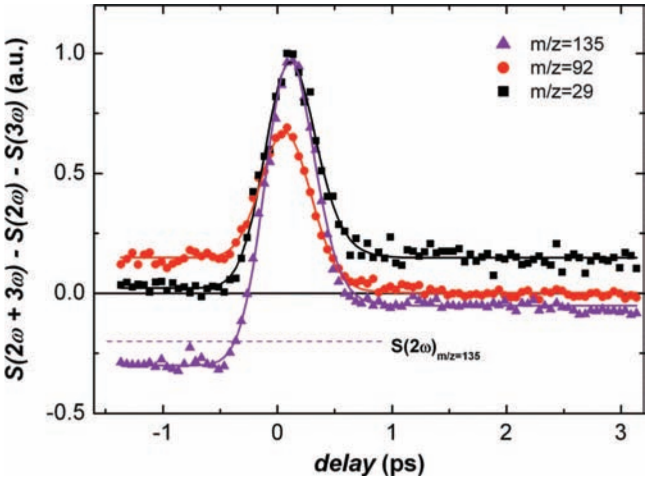

Figure 3. Parent and fragment ion transients (source pressure 2×10^{-7} mbar). A positive time delay corresponds to initial pumping by 3ω (280 nm) and subsequent probing by 2ω (420 nm). For each mass the baseline corresponds to the sum of the signals induced by the pump and the probe, individually.

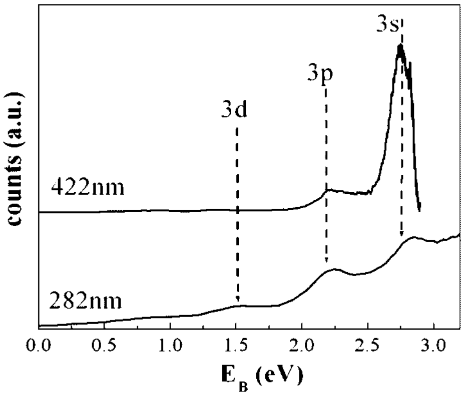

Figure 4. One-color photoelectron spectra obtained with 2ω photons (top) and 3ω photons (bottom).

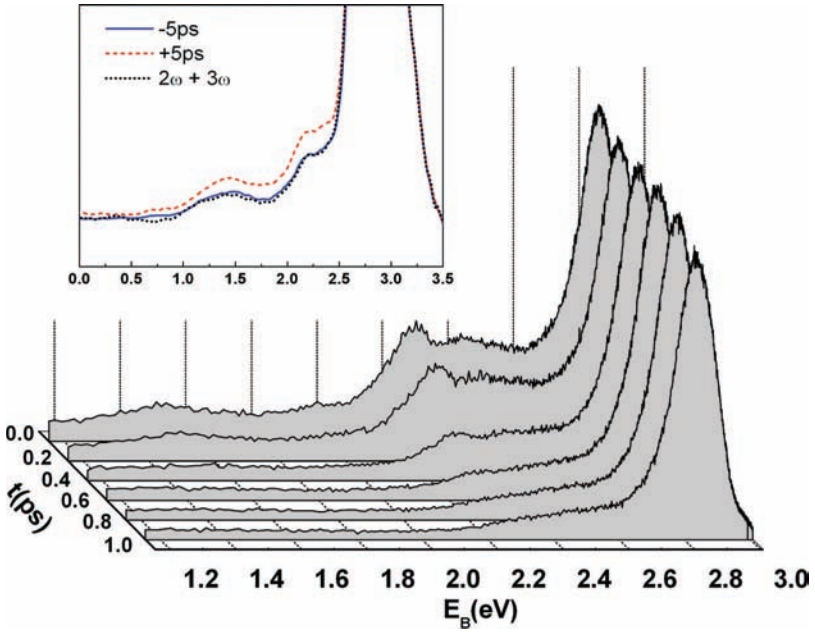

Figure 5. Time-resolved photoelectron spectra at various time-delays (source pressure 2×10^{-7} mbar). Positive time means 3ω excitation and 2ω ionization. The evaluation of the binding energy assumes the ionization by one pump photon (negative times) or one probe photon (positive times). The insert shows the photoelectron spectra at -5 and $+5$ ps delay together with the sum of the single-color spectra. A higher intensity was required in order to observe the small difference signal.

If the molecule does absorb a single 3ω photon it will quickly loose a chlorine atom to form the nitrogen based radical that is shown in eq. (1). The energy difference between the ground-state chloroamine and the product radicals calculated at the G3(MP2) level[13] is 2.5 eV. Thus, the photon induced bond breakage will deposit a substantial amount of energy into the radical (less than or equal to $h\nu_{3\omega} - 2.5 \text{ eV} = 1.9 \text{ eV}$). The ionization energy of the radical is 8.8 eV and it will therefore require three 2ω photons or two 3ω photons to ionize it. However, this is an upper bound since the radical will most likely be highly vibrationally excited.

Time-Resolved Mass Spectrometry. The photon-induced mass spectra of *N*-chloro-*N*-ethylbutylamine are shown in Figure 2a (280 nm) and Figure 2b (420 nm).

It can be seen that the principal fragment peaks correspond to loss of a chlorine atom (35 u or 37 u) and a propyl radical (43 u). As on many previous occasions, it is not immediately obvious whether the decomposition has occurred from the neutral parent molecule or from the ionized *N*-chloro-*N*-ethylbutylamine; both fragmentation patterns are very probable processes of such radical cations.

The two-color mass spectra have peaks in the same positions as their one-color equivalents; they only differ by the intensity of the mass spectral peaks. The temporal evolution of the *m*/*z* 29 (ethyl cation), of *m*/*z* 92 (propyl loss from the parent ion), and of the parent ion *m*/*z* 135 is shown in Figure 3.

The transients are adjusted so that the baseline (0.0 level) corresponds to the sum of the signal induced by the pump and the probe, individually. The parent ion current that results from the 2ω photons alone is also included for reference. The parent ion current is depleted at negative times with respect to the 2ω signal whereas the fragment ion current (*m*/*z* 92) is enhanced. At positive times the scenario is similar but the amplitude of the time-dependent signal is significantly smaller in the case of *m*/*z* 92 and *m*/*z* 135 whereas there is a significant enhancement for *m*/*z* 29. Around time-zero an enhancement is observed; in both the case of the fragment and parent ion transients the behavior is pulse limited (<400 fs). All of the remaining fragment ion transients that give rise to sufficient signal show a behavior similar to either that of *m*/*z* 92 or to that of the parent ion, only the signal is significantly smaller. The time dependence of the *m*/*z* 100 ions, i.e., the ion that could result from ionization of the product radical after the loss of a chlorine atom, is similar to that of the parent. However, the ion yield is highly nonlinear as a function of the pressure in the interaction region. The effect is illustrated in Figure 2, parts b and c, where the mass spectra are shown at different source pressures; the higher the source pressure the higher the yield of *m*/*z* 100. This suggests that the formation of *m*/*z* 100 is not from the ionization of the neutral radical. Instead, it is of bimolecular origin and could be due, for example, to collisions between neutral molecules and the parent ions in the interaction region, or dimers.

Time-Resolved Photoelectron Spectroscopy. The photoelectron spectra that arise from excitation with the 2ω and 3ω pulse, respectively are shown in Figure 4. We note that the ratio of peak intensities depends strongly on the excitation wavelength, reflecting the different excitation pathways to the Rydberg states. From the experimentally determined binding energies of the electrons ($E_{\text{photon}} - E_{\text{kin}}$), we obtain state energies of 5.9 eV, 6.4, and 7.1 eV. These agree very well with the calculated energies of the vertical Rydberg transitions in Figure 1. Thus, we assign the photoelectron peaks in the single-color spectra to excitation to the Rydberg manifold (3s, 3p, and 3d) with two 3ω photons and three 2ω photons, respectively, and subsequent ionization.

The photoelectron spectra at various time-delays are shown in Figure 5.

The two-color signal around $t = 0$ produces a substantial amount of features over the entire range as a result of the multiple combinations of 2ω and 3ω photons. All of the distinct peaks have a pulse-limited behavior and must be associated with the $t = 0$ enhancement of the ion transients. From the insert it can be seen that there is no persistent photoelectron signal at negative times. This means that the processes that give rise to the persistent components of the ion transients at negative times do not produce any photoelectrons. However, at positive times we do observe a very small broad persistent feature (insert of Figure 5) that extends over the entire range up until electron kinetic energies approximately equal to that of a 2*ω* photon. The only ion transient that was found to show enhancement at positive times was that of *m*/*z* 29. Therefore, the process that gives rise to this particular fragment must be the one associated with the broad photoelecton feature.

Unraveling of the Processes Induced by 2*ω* and 3*ω* fs Pulses: Combining Calculations, Time-Resolved Photoelectron Spectroscopy and Mass Spectrometry. To account for the existence of a two-color ion signal and the absence of a two-color photoelectron signal at negative times we suggest that three 2*ω* photons generate an ion that is then excited by a 3*ω* photon to induce decomposition and therefore depletion of the parent ion signal and enhancement of the fragment ion signal. Since the ions are already generated by the 2*ω* pulse the 3*ω* pulse does not generate any electrons This is in line with the potential energy surfaces in Figure 1: a single 2*ω* photon does not match any state and it is difficult to prevent multiphoton ionization under the laser flux of the experiment ($\sim 10^{13}-10^{14}$ W/cm^2). We note that the persistent depletion and enhancement at negative times is indeed a two-color phenomenon as the baseline of the transients in Figure 3 represent the sum of the individual contribution of the 2*ω* and 3*ω* beams. Thus, the temporal features of the ion transient at negative times have nothing to do with the dynamics of neutral molecules—they are solely associated with excited states ions.

At positive times the scenario is different; in this case there is a match between the behavior of the time-resolved mass and photoelectron spectra. We do observe a very broad and persistent photoelectron signal and an enhancement in the transient of *m*/*z* 29. We attribute the time-resolved signal to result from the 3*ω* excitation to the S_1 state. The calculations in Figure 1 show that the energies match and that S_1 is repulsive, so that the excitation can lead to the ultrafast formation of a radical. The energy difference between the ground-state chloroamine and the product radicals is 2.5 eV, thus, by assuming no kinetic energy for the chlorine atom, up to 1.9 eV will be deposited in the radical. Given that the electronic nature of the radical and the resulting ion are very different, the ionization of the hot radical can lead to photoelectrons with a very broad distribution of kinetic energies. The resulting ions ($CH_3CH_2NCH_2$-$CH_2CH_2CH_3^+$) will be quite hot and can decompose to form ethyl cations by a simple C—N bond cleavage in the acceleration region of the mass spectrometer. The time dependent *m*/*z* 29 signal thus reflects the (long) lifetime of the neutral radical, this was verified by investigating time delays up to 100 ps.

4. Conclusions

In femtosecond resolved studies of gaseous molecules the use of an ionizing probe has been widespread. Time-resolved mass spectrometry is a convenient technique as almost all molecules can be ionized through multiphoton ionization. The apparent drawback is that the origin of the fragment ions can be ambiguous. We have shown that this is not the only caveat as the present study has revealed that excited-state ions can also be in play. The evidence is unambiguous since we observe a distinct temporal evolution of the ion current but no photoelectrons to match. This means that the process associated with the ion time dependencies does not involve ionization. The first pulse ionizes the molecules directly and the second (delayed) pulse is absorbed by the already present ions to induce ionic decomposition. This behavior is complicating studies of neutral molecule dynamics in systems where, due to low absorption cross sections, one has to resort to high laser power to achieve an appropriate experimental signal, because it is difficult to avoid multiphoton ionization. A related observation was recently discussed for acetone.[6] We also find evidence for the direct ionization of the (long-lived) radical that is being formed as the result of ultrafast bond breakage on the repulsive S_1 surface but, again, the associated ion has decomposed and an inspection such as the one we have conducted presently of the time-resolved photoelectron spectra is required.

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References and Notes

(1) Upadhyaya, H. P.; Kumar, A.; Naik, P. D. *J. Chem. Phys.* **2003**, *118*, 2590.

(2) Diau, E. W. G.; Herek, J. L.; Kim, Z. H.; Zewail, A. H. *Science* **1998**, *279*, 847.

(3) Brogaard, R. Y.; Sølling, T. I. *J. Mol. Struct. (THEOCHEM)* **2007**, *811*, 117.

(4) Ihee, H.; Goodson, B. M.; Srinivasan, R.; Lobastov, V. A.; Zewail, A. H. *J. Phys. Chem. A* **2002**, *106*, 4087.

(5) Gosselin, J. L.; Minitti, M. P.; Rudakov, F. M.; Sølling, T. I.; Weber, P. M. *J. Phys. Chem A* **2006**, *110*, 4251.

(6) Rusteika, N.; Møller, K. B.; Sølling, T. I. *Chem. Phys. Lett.* **2008**, *461* (4−6), 193–197.

(7) Taylor, D. P.; Goode, J. G.; LeClaire, J. E.; Johnson, P. M. *J. Chem. Phys.* **1995**, *103*, 6293.

(8) LeClaire, J. E.; Anand, R.; Johnson, P. M. *J. Chem. Phys.* **1997**, *106*, 6785.

(9) Johnson, P. M.; Anand, R.; Hofstein, J. D.; LeClaire, J. E. *J. Electron Spectrosc. Relat. Phenom.* **2000**, *108*, 177.

(10) Neale, R. S.; Walsh, M. R. *J. Am. Chem. Soc.* **1965**, *87*, 1255.

(11) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*, 2nd ed; Prentice Hall: Upper Saddle River, NJ, 1999.

(12) Pedersen, S.; Zewail, A. H. *Mol. Phys.* **1996**, *89*, 1455.

(13) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. *J. Chem. Phys.* **1999**, *110*, 4703.

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