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ARTICLES

Investigation of Ion−Molecule Reactions *via* Femtosecond Excitation and Ionization of [Tetrakis(dimethylamino)ethylene]$_{n\geq 1}$

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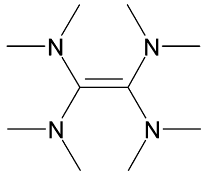
The dynamics of ionic monomer and multimers of the ethylenic molecule TDMAE (tetrakis(dimethylamino)ethylene) have been studied under femtosecond stepwise excitation using an energy surface of the neutral molecule (or cluster) as a relay. This specific excitation takes advantage of the wave packet evolution in the neutral intermediate state to (i) allow access to different regions of the ionic potential surface and (ii) identify some aspects of the dynamics in the ionic state of either TDMAE$^+$ or TDMAE$_n{}^+$. This original experimental approach we shall name double pump excitation. We have identified the existence of a double well in TDMAE$_n{}^+$ corresponding to a different localization of the positive charge, the most stable corresponding to a complete delocalization over the nitrogen atoms. A reaction in the dimer and higher multimer ions is observed that involves the formation of compounds of general mass 200$_m$116$_n{}^+$. This reaction is only observed in clusters and not in thermal ion molecule collisions between TDMAE$^+$ and TDMAE. A tentative mechanism of formation for this product is proposed that involves the creation of a distonic ion via H-atom migrations. The double pump method could be extended to many other systems to explore competing pathways in ionic reactions, differently accessed via transient states of a neutral intermediate.

I. Introduction

Ion molecule reactions represent an essential class of gas-phase reactions, on fundamental and practical grounds. These reactions have typically been investigated in collisions. In turn, a powerful approach of the chemical dynamics of reactions is provided by time-dependent, femtochemical methods where the reagents are prepared within a cluster by a pump laser and the fragments are probed by a second ultrashort laser, as demonstrated on neutral clusters.[1] This allows for the exploration of the potential energy surfaces of the reacting pair and could be also accomplished on ionic clusters. However there have only been few such examples in the case of ion molecule reactions.[2] This is due to the difficulty of probing the intermediates or the product ions in such reactions.

We propose here a femtosecond approach to ion molecule reactions, where we do not detect this time-dependent evolution. Rather, femtosecond excitation is used to prepare different regions of the potential energy surface in an ion−molecule reaction, via an excited intermediate state of the neutral cluster, which undergoes ultrafast evolution. The conditions of the preparation affects the final states of the ionic products. More precisely, a first femtosecond pulse prepares the system on a neutral intermediate surface and creates an evolving wave packet moving rapidly downhill to a lower excited surface; in this way, the system explores much of the configuration space. In general, because of the frozen geometry of clusters, cluster-induced reactions have the property of severely limiting the available phase space for the reaction. Here, instead, by the addition of a temporal switch, we intend to tune that dimension: a second femtosecond pulse will promote the system above the ionization potential after a delay with the first pulse. The variation of this delay will allow a tuning of the region accessed on the ion surface. Hence, the first femtosecond pulse initiates a transformation of the excited neutral cluster that is transferred to the ion cluster via the second pulse. Such a two-pump experiment could be compared with the two-pulse preparation scheme reported by Radloff et al..[3]

We report here the observation of reactions in the ionic monomer and the ionic multimers of the title molecule, tetrakis(dimethylamino)ethylene (TDMAE) of structural formula



resulting in the formation of several ionic products. Some of these reactions will be interpreted as driven by the formation of distonic ions and hydrogen migrations. Reactions involving

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several TDMAE units will be shown to occur only in clusters carrying some excess energy, not in full collisions at low energy between $TDMAE^+$ and a neutral TDMAE molecule, indicating that energy barriers are present along the reaction paths. The full collision experiments have been performed in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). Intracluster and intramolecular ion−molecule reactions have been activated by laser ionization of the neutral cluster, either by a single photon or in a stepwise manner, via an intermediate resonant state, applying the femtosecond two-pump excitation technique introduced above.

The TDMAE molecule was selected for its reported low ionization energy, 5.4 eV,[4] due to the dimethylamino groups and for its ultrafast electronic relaxation, common to ethylenic compounds.[5] We have reported in a previous paper the mechanisms of the electronic relaxation of free TDMAE, from the very initial step in the Franck−Condon zone, down to a fluorescent state, over widely different time scales, from the femtosecond to nanosecond times.[6] We have described these relaxation pathways in terms of generic properties of the excited states of double bond molecules exemplified by ethylene. With a femtosecond pump at 266 nm (4.6 eV), a wave packet is formed that initiates a rapid downhill movement along the slopes of the excited potential energy surface. The wave packet prepares initially a planar geometry of the molecule with a valence configuration $V(\pi\pi^*)$. Then it moves in 300 fs toward a conical intersection where the molecule is deformed and gets a zwitterionic character $Z(C^+C^-)$, which subsequently decays with a 120 ps time constant to a charge transfer state CT. This latter state has the positive charge delocalized on the dimethylamino groups. With a pump at 200 nm (6.2 eV), the free TDMAE molecule is excited 0.8 eV above the ionization limit and a competition is observed between ionization and relaxation at this energy. The wave packet movements that have just been recalled in excited neutral TDMAE is the tool used in the present work to tune the dissociation of the $TDMAE^+$ ion. Similarly, considering the excited TDMAE multimers as locally excited on a single monomer moiety, the same wave packet movements are used to tune the intracluster reactions of the multimer ions.

The ionic state dynamics of the TDMAE molecule and the TDMAE clusters observed in the present work revealed a competition between reaction and evaporation processes. Several types of experiments have been combined to explore these mechanisms:

(1) Femtosecond two-pump experiments are performed on the free TDMAE molecule with a couple of wavelengths 200 + 800 nm and a high intensity of the second pump laser, resulting in multiphoton ionization and formation of specific ionic fragments that have not been reported so far.

(2) "Nontime-resolved" collisions between $TDMAE^+$ ions and neutral TDMAE gas are explored in a FT-ICR spectrometer. This experiment was performed to reveal energy barriers along the reaction path and to set limits to the association energy of the $TDMAE^+$, TDMAE pair.

(3) Direct femtosecond ionization of the $TDMAE_n$ clusters at 200 nm (6.2 eV) is forming reaction products and evaporated clusters.

(4) Femtosecond two-pump experiments are performed on the $TDMAE_n$ clusters, with a first laser at 266 nm (4.6 eV) and a second at 800 nm (1.5 eV). The same energy was applied with the single 200 nm pump photon above, but here, the use of a double-pump pulse with a time delay between both allows initiation of the ionic processes from various locations of the ionic energy surfaces. This is the most important part of the present investigation.

II. Experimental Section

II.1. Femtosecond Experiments in TDMAE. The experimental apparatus used for the real time experiments associates a pulsed supersonic beam of TDMAE seeded in helium with a time-of-flight mass spectrometer (TOF-MS). It is coupled to the LUCA femtosecond laser facility of Saclay, to perform the femtosecond two-pump experiments.

The fundamental of a titanium-sapphire regenerative amplifier at 800 nm is used with a 20 Hz repetition rate as the second pump. The third (266 nm) or fourth (200 nm) harmonic is used as the first pump. The harmonic outputs of the laser are passed through a delay line, which allows us to vary the delay between them and the 800 nm laser pulses. At the end, the two beams are quasi-collinear, perpendicular to both the TOF-MS and the molecular beam.

The cross correlation widths of the laser pulses are respectively 120 and 140 fs for the 266/800 nm and 200/800 nm pump combinations. They have been determined by two methods: at 266 + 800 nm, the ionization of butadiene is purely nonresonant and the ion signal reproduces the cross correlation of the lasers, whereas, with the 200 + 800 nm couple of wavelengths, the ionization of ammonia proceeds through an intermediate level of decaying in 39 fs.[5]

The pulse intensities that are injected into the machine are, respectively, 20−100 μJ, 10 μJ, and 1−5 μJ at 800, 266, and 200 nm. The first pump laser at 266 or 200 nm is unfocused to perform the excitation of the TDMAE molecule or of its multimers via a single-photon process. Then the ionization to $TDMAE_{n\geq 1}^+$ by the second laser is achieved with one or several photons. In the cluster experiments ($n \geq 2$), the second pump beam is mildly focused to achieve ionization in a sufficiently low field, typically 2×10^{11} W cm^{-2}.[7,8] Nevertheless, as we shall see below, this energy density is large enough to allow for two-photon ionization in several cases. In the free TDMAE experiment ($n = 1$), the second pump beam is more tightly focused to allow for a multiphoton ionization of higher order.

The supersonic beam has already been described in a previous paper.[6] It proceeds from a TDMAE/helium gas mixture through a pulsed nozzle. The multimers of TDMAE are produced with increasing backing pressures of helium in the molecular beam. The temperature of the TDMAE vessel is maintained at room-temperature resulting in a vapor pressure of 0.35 Torr that is drifted to the supersonic expansion by the flowing backing gas.

The signals are the ion intensities corresponding to the mass of each ionic product, detected using a time-of-flight mass spectrometer (TOF-MS). They are recorded as a function of the delay between the laser pulses in time steps multiple of 0.67 fs. They are analyzed in a sequential three-level scheme (see ref 5 and references therein). A level A initially populated, by the pump pulse decays at rate $k_A = 1/\tau_A$, into a level B which further decays into C at rate $k_B = 1/\tau_B$. If we call σ_A and σ_B the efficiencies for the ionization of levels A and B to a given M^+ ion, we can simulate the corresponding signal $S(t)$ with

$$S(t) = \sigma_A e^{-t/\tau_A} + \sigma_B \frac{\tau_B}{\tau_B - \tau_A}(e^{-t/\tau_B} - e^{-t/\tau_A}) \text{ for } t > 0$$
$$S(t) = 0 \text{ for } t < 0 \qquad (1)$$

$S(t)$ is convoluted with the cross correlation function of the two lasers for comparison with the experimental data. The ion signals at a given mass can result from several such processes acting in parallel. This happens for instance when observing multimers at a mass channel that sums intact multimers and evaporated multimers. In that case, $S(t)$ has to be summed over all relevant channels, $S(t) = \Sigma_i S_i(t)$, where each component can have a different set of decay constants (τ_{Ai}, τ_{Bi}) and ionization cross sections (σ_{Ai}, σ_{Bi}).

II.2. ICR Experiments. The full collision experiments between TDMAE$^+$ ions and TDMAE molecules were performed with the FT-ICR (fourier transform ion cyclotron resonance) mass spectrometer "MICRA" (mobile ICR analyzer), recently built in the Orsay laboratory.[9,10] In the ICR general technique, ions are stored in a Penning trap, a combination of magnetic and electric fields. Excitation of the cyclotron movement of the ions increases the radius of their orbit in the trap allowing both for their selection (undesired ions are collided on the trap walls) and for their detection. The latter is achieved by recording the signal induced in electrostatic plates by the periodic movement of the trapped ion packet. A Fourier transform yields to the cyclotron frequency of the ions present in the trap, which is inversely proportional to their mass-to-charge ratio. FT-ICR mass spectrometers are routinely used either for reactive collision studies or for high-resolution mass spectrometric analysis of large biomolecules.[11−13] Concerning ion−molecule reactivity studies, the strong points of the FTICR technique are the following: (i) since the ions are trapped, the successive chemical processes taking place in an ion−molecule system are observed over a wide time range (a few milliseconds to minutes); (ii) chemical reactions can be studied at thermal energy, since in the ICR cell no kinetic energy is given to the trapped ions.

The spectrometer MICRA is a compact FT-ICR apparatus based on the use of a cylindrical permanent magnet assembly providing a nominal field of 1.25 T with a high homogeneity. It provides us with high mass resolution, ca. 70 000 at mass 200. The ICR cell is equipped with an optical access and two pulsed gas inlets. Experimental sequences including admittance of neutrals, electron ionization, mass selections, ion−molecule reactions, and relaxation delays can be designed for the selective preparation of various ions followed by spectroscopy or reactivity studies.

The TDMAE gas is first introduced into the MICRA chamber and is ionized by 70 eV electrons. Then, the remaining neutral gas is pumped down, and the desired TDMAE$^+$ ions are mass selected. Afterward, the TDMAE gas is introduced again in the trap, as a reactive gas, at pressures ranging between a few 10^{-7} Torr and 3×10^{-6} Torr. For a given reactive gas pressure, the reaction time was varied from 1 ms to 60 s. The reactant gas is then pumped down before final detection.

Results

III.1. Two-Pump Experiment on Free TDMAE$^+$. We first examine the fragmentation of TDMAE$^+$ ions in the two-pump experiment. The wavelength of the first pump is 200 nm (6.2 eV), and that of the second pump is 800 nm (1.5 eV). Standard pump−probe experiments have been reported in ref 6 using the same couple of wavelengths as present, 200 nm for the pump and 800 nm for the probe. The focus in ref 6 was to study the dynamics of the excited intermediate state populated by the pump laser. Surprisingly, although the pump photons excite the TDMAE molecule above its adiabatic ionization energy, a transient ionization signal is observed with the probe laser. As discussed in ref 6, this is the indication that ionization of TDMAE by the pump laser is not a direct process; instead it has a low efficiency and proceeds through an autoionization step that competes with the production of neutral excited states of TDMAE. In this former study, the decaying intermediate state of TDMAE was probed by observing either the parent TDMAE$^+$ ion (mass 200 amu) or fragment ions at masses 45, 58, 88, and 102 amu. For energy reasons, these ions are produced following absorption of 2 × 800 nm probe photons.

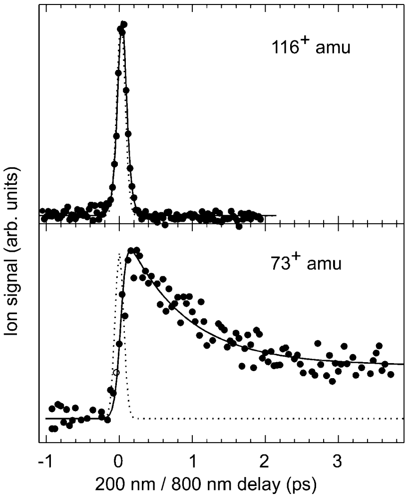


Figure 1. Evolution of the ion signal measured at mass 116 amu (top panel) and 73 amu (bottom panel) as a function of the delay between the first pump (200 nm) and the second pump (800 nm) delay in the two-pump study of free TDMAE. The dotted curve in both panels is the cross correlation function of the lasers, whereas the full curve is a fit using expression 1. The horizontal scale is the same in both panels.

In the present work, the laser of 800 nm wavelength can be more focused, and ions of 73 and 116 amu are observed. Since these ions are not observed at lower focusing of the second pump laser, they are exclusively produced by the absorption of at least three 800 nm photons from the intermediate excited level populated by the first pump laser at 200 nm. These new results are shown in Figure 1. The ion signal at mass 116 amu is slightly asymmetric and suggests a very fast decay of ∼20 fs. No plateau or decay follows. In contrast, the transient ion signal at 73 amu has a much longer decay time, 1000 ± 200 fs, that is followed by a plateau. Unfortunately, the reduced signal-to-noise ratio at 73 amu does not allow us to determine whether the signal has a nonzero rise time.

III.2. ICR Experiments Probing TDMAE + TDMAE$^+$ Collisions. Under the experimental conditions described in section II.2, no reaction or association reaction of TDMAE$^+$ ions with neutral TDMAE was observed. According to calibrations performed on the MICRA apparatus through measurements on other systems,[10,14] the absence of an association reaction forming TDMAE$_2{}^+$ under regimes where multiple collisions are occurring allows us to propose an upper limit of 0.8 eV to the binding energy of the TDMAE-TDMAE$^+$ dimer ion. The absence of other reaction products indicates that if reactions are energetically possible, energy barriers are present along the reaction paths that exceed energies accessible in room-temperature collisions.

III.3. Single-Step Ionization of the Multimers of TDMAE at 200 nm. The excitation of multimers by a single UV photon at 200 nm places them above the adiabatic ionization potential of free TDMAE. At low backing pressures, 1.5 and 2 bar, only few higher masses as that of TDMAE appear in Figure 2: mass 400 (the dimer ion), mass 316, and mass 432 very weakly. The intensity of the dimer is only a few percent that of mass 316. The origin of the latter mass, 316, is assigned to a reaction product formed after the ionization of TDMAE multimers. This

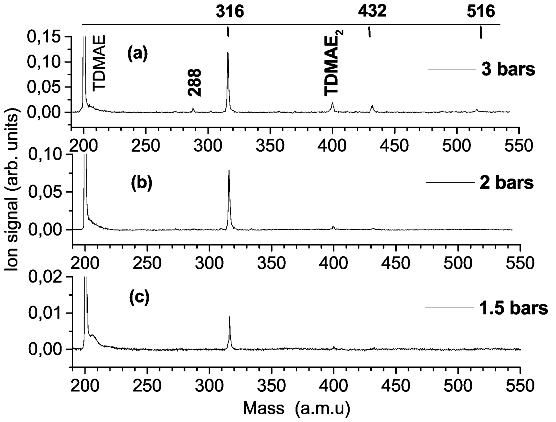


Figure 2. Mass spectrum observed upon single-photon ionization of the TDMAE beam with a 200 nm femtosecond pulse at three different helium backing pressures. The intensity of the TDMAE parent ions at mass 200 amu has been normalized to 1.

is confirmed by a negative experiment performed under the same laser conditions in an effusive beam. There, no clusters are present and no ions of mass 316 are observed. This somehow double-checks the information gained in the previous section. We thus infer that the formation of the product with mass 316 is due to a reaction between $TDMAE^+$ and TDMAE within multimers.

Ions of higher mass are detected when the backing pressure is increased, as illustrated in Figure 2. The absolute intensity of masses 316, 400, and 432 increases with the backing pressure when varied from 1.5 to 3 bar, while mass 516 is only seen at 3 bar. The ion signals at masses 316 and 432 increase linearly with the backing pressure of helium in the molecular beam. The largest cluster observed with a sufficient resolution, in our experiments, is the tetramer ($m = 800$ amu, not shown in the figure), at pressures of ca. 5 bar of helium. Other mass peaks are also detected between the peaks of the TDMAE clusters with masses $(200)_n{}^+$. This corresponds to reaction products within ionic multimers. Their general mass is $(200_n116_m)^+$. The intensity ratio between the reaction products and the next higher multimer is always in favor of the reaction product.

The temporal evolution of multimers and products has been checked after a 200 nm excitation, using a probe at 800 nm. In contrast to the TDMAE monomer experiment reported above, only a weak transient signal was observed at any mass. Hence it is not further detailed. The lack of an intense transient signal is attributed to the high excess energy imparted to the cluster by the probe, causing its evaporation and its transfer to the signal at the mass of the monomer.

III.4. Sequential Excitation of Multimers with 266 and 800 nm and Time Dependence. We first present an overview of the masses created with the 266/800 nm excitation scheme, at increasing helium backing pressures. The mass spectra shown in Figure 3 have been integrated for all laser delays between 0 and 300 ps. They have been taken at 1.5 and 5 bar pressures.

At 1.5 bar pressure of helium, few masses are observed: the dimer ion (400 amu) and the fragment ion at 316 amu. When the helium backing pressure was increased up to 5 bar, peaks of higher masses become significant, such as the trimer $TDMAE_3$ (600 amu) and reaction products at general mass values of $(200_n116_m)^+$ (namely 316, 432, 516, and 548 amu). The other peaks, marked with an asterisk in Figure 3, result from high order multiphoton absorption of the 800 nm photons, since they strongly depend on the laser energy. They are not considered further.

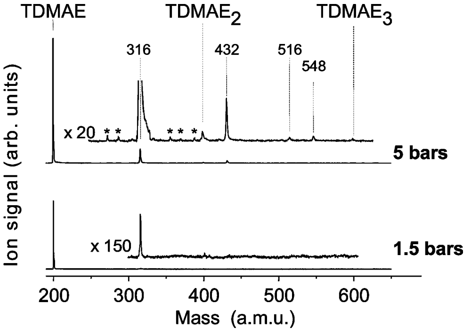


Figure 3. Mass spectrum of the TDMAE beam observed at two different pressures, 1.5 bar (bottom panel) and 5 bar (top panel). It was obtained with the double-pump excitation at 266/800 nm after summing all delays between the two-pump laser pulses. The peaks of the 5 bar mass spectrum that are labeled with an asterisk are due to the ionization of the $TDMAE_n$ clusters by more than two 800 nm photon ionizations and result from reactions of highly excited species.

TABLE 1: Evolution of the Transient of 300 fs When Increasing the Helium Backing Pressure in an Experiment Where the $TDMAE^+$ Ion is Recorded as a Function of the Pump (266 nm) and Probe (800 nm) Delay

helium backing pressure (bar)	decay constant (fs)
1	300
3	260
5	220
7	200

III.4.1. Time Evolution of Mass 200, TDMAE. The time evolution of the $TDMAE^+$ ion (200 amu) has been recorded at different backing pressures of helium as a function of the 266/800 nm delay. Small clusters can evaporate in the ionization region of the TOF-MS. Hence, recording 200 amu ions probes also indirectly the evolution of small TDMAE clusters.

At low backing pressures, when no or few TDMAE clusters are present in the beam, the TDMAE ion signal decays in 300 fs to reach what is seen as a plateau at femtosecond time scales.[6] When the pressure is increased, the value of the decay constant decreases to reach a value of 200 fs at high pressures of helium, when the molecular beam produces large TDMAE clusters. These results are summarized in Table 1.

III.4.2. Time Evolution of the TDMAE Multimers of Mass 200_n. When the backing pressure in the molecular beam is increased, clusters of TDMAE detected at multimer ion masses ($n \times 200$ amu) are observed. Their time evolution has been recorded as a function of the 266/800 nm delay. The time evolution measured at the dimer ion mass, 400 uma, is presented in Figure 4 for three different pressures. It can be understood as the superposition of two components, the relative importance of which varies with the helium backing pressure:

(1) At low pressures, when the mass spectrum reveals only the dimer, together with the reaction ion product at 316 amu, only one exponential decay of 40 ± 20 fs is assumed.

(2) When the pressure is increased to 3 bar, the trimer (mass 600) appears and displays the same 40 fs time constant. At the same time, in the decay of the dimer, a second component of longer time constant, 200 ± 20 fs, superimposes on the shorter 40 fs decay. The curve fitting of the experimental points in the middle panel of Figure 4 has been simulated by the sum of two independent exponential decays, 40 and 200 fs, convoluted by the cross correlation of the two laser beams. The corresponding contributions of these decay components are shown in this figure.

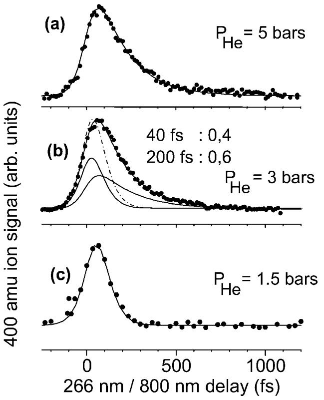


Figure 4. Evolution of the ion signal at mass 400 amu as a function of the delay between the two pumps at 266/800 nm. The panels a−c correspond to three helium backing pressures as labeled in the figure. The solid line passing through the experimental points is a fit using a single exponential in expression 1 ($\sigma_B = 0$). The best fit is obtained with $\tau_A = 40$ fs in panel c and $\tau_A = 200$ fs in panel a. Panel b was fitted by the sum of two single exponential decays, 40 and 200 fs, for which contributions are indicated as full curves in the figure. The dot−dashed curve shows that a fit with the sole 40 fs contribution is clearly not sufficient.

At 5 bar and higher pressures, multimers of TDMAE up to the observation limit of $n = 4$ are observed. This suggests that clusters of even larger masses are present in the beam. Under these experimental conditions, only the component of 200 fs is observed in the signal measured at the dimer ion mass. Moreover, all the multimers of TDMAE detected up to mass 800 present the same time constant of 200 fs, which appears as a single exponential.

The relaxation of TDMAE clusters has also been investigated at long time scales. This is justified by the observation of a long-lived state of 120 ps in free TDMAE, corresponding to the excitation of the zwitterionic state by 2 × 800 nm probe photons.[6] No such long time decay has been detected at the multimer ion masses $n \times 200$. This result is further confirmed by similar experiments achieved with nanosecond pulses (266 nm pump/532 nm probe) where no such ions have been detected.

III.4.3. Time Evolution of the Reaction Products of Mass 200_m116_p. With the 266/800 nm two-pump excitation, reaction ion products of mass $(200_m116_p)^+$ are observed. Note that the writing of $(200_m116_p)^+$ is simply for convenience and does not imply anything about the structure of the cluster ion. Their time signatures of these ions have been measured as a function of the delay between the two laser pulses. They are very similar, within experimental error. Specific emphasis is therefore placed upon the most intense ion product at mass 316 amu ($m = 1$, $p = 1$). The results are shown in Figure 5. The two top curves correspond to the 3 bar backing pressure experiment. The bottom curve was obtained at 1.5 bar. The observed decay extends from the femtosecond to the nanosecond scale in the 3 bar experiment. Two successive time evolutions are apparent, a short decay, 200 ± 20 fs, which is better viewed with the scale of the top panel in the Figure 5 curve, and a long decay with a time constant greater than 500 ps that appears better in the middle panel of the figure. The latter "close-to-nanosecond" time constant was confirmed by nanosecond experiments with 266/532 nm double-pump excitations and delays of several nanoseconds. This slow component does appear also, but very weakly, in the 1.5 bar experiment (see the bottom curve in Figure 5).

The intensity ratio between the above short- and long-time decays not only depends on the helium backing pressure but also varies with the intensity of the probe. As we have described previously,[6] the observation of long decays relates to the formation of the Z state or the lower charge transfer states which are ionized with two 800 nm photons.

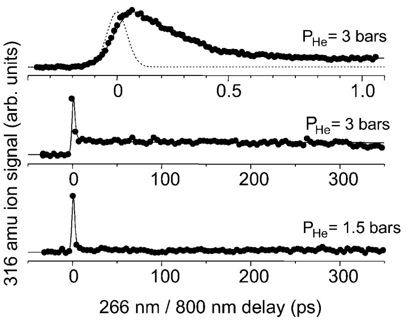


Figure 5. Evolution of the ion signal at mass 316 amu as a function of the delay between the two pumps at 266/800 nm. Data taken with a 3 bar helium backing pressure are shown in the top and middle panels, whereas data taken at 1.5 bar are reported in the bottom panels. The horizontal scale is picosecond for the middle and bottom panels. The top panel is a zoom at a femtosecond time scale of the 3 bar data. The full curve passing through the experimental points is a fit using expression 1 with $\tau_A = 200$ fs and $\tau_B > 500$ ps. The cross correlation function of the lasers is shown as a dotted curve in the top panel.

III.4.4. Time Evolution of Cluster Fragments of Other Masses. The temporal evolution of the ionic reaction products at masses 273, 288, and 302 amu has also been recorded. It is recalled that these fragments need a higher energy density of the 800 nm laser to appear. Although the ion signals are weak, always less than 1% of the TDMAE ion signal, the signal-to-noise ratio for the time dependencies are good. The measured transient signal at these ion masses is similar to that encountered above at mass 316 amu: a rapid decay, 200 ± 20 fs, followed by a very slow one that appears almost as a plateau. The height of the latter, relative to the initial rapid transient, depends on the fragment, the probe intensity, and the size of the initial clusters.

IV. Discussion

In section III, the observation of various decay channels of free TDMAE and of the TDMAE multimers following ionization has been reported: intraionic reaction in the free TDMAE experiment; evaporation of neutral monomers and ion−molecule reactions in the multimer experiment. The stepwise ionization of either monomers or the multimers shows a rich time evolution of the ionic products, which reflects, as anticipated in the Introduction, the wave packet motion in the intermediate state of neutral species that is accessed by the first pump laser.

For convenience, we initiate the discussion by considering evaporation phenomena in the multimer experiment. This reveals an important property of the $TDMAE^+$ moiety in the $TDMAE_n^+$ multimers. Then we discuss ionic reaction processes, first within free $TDMAE^+$ ions, then within $TDMAE_n^+$ cluster ions. We shall see that the reactive processes are quite complicated and involve many bond rearrangements. From comparison with other systems, we shall anticipate indeed that H-atom shifts are steering the reactions. The full interpretation of these processes should go through ab initio calculations of potential energy surfaces involving at least three deformation coordinates of the $TDMAE^+$ ion, plus coordinates that enable the H-atom transfer processes. Such calculations are far beyond the scope of the present work. Therefore, the discussions that follow provide qualitative anticipations of what these reactive potential energy surfaces could be, using the present experimental information as guidelines.

Before these discussions, energy considerations must be made that concern the cluster experiment.

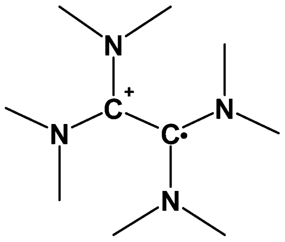
IV.1. Energy Disposal in the $(TDMAE)_n^+$ Cluster Ions. The multimer ions immediately after their formation by the second pump laser are considered as locally ionized. The $TDMAE_n^+$ ions are formed, following absorption of 4.65 eV (266 nm) + 1.55 eV (800 nm) = 6.2 eV photons, by neutral $TDMAE_n$ clusters. Part of this energy is used to ionize the neutral multimer, and the remaining is shared between kinetic energy in the outgoing electron and excess energy in the ion. The maximum excess energy (called simply excess energy hereafter) that can be transferred to the $TDMAE_2^+$ is estimated now.

Estimating the excess energy of the $TDMAE_2^+$ ion after ionization of neutral $TDMAE_2$ is achieved by a Born−Haber cycle and the three following inputs. First, the adiabatic ionization potential of the free TDMAE ion is 5.4 eV.[4] Second, an estimate of ca. 0.4 eV can be assumed for the ionic dimer $TDMAE^+$−TDMAE. It is reasonable indeed to suppose that it is smaller than the binding energy of the ethylene dimer ion (0.68 eV);[15] in ethylene indeed, the binding attraction arises from the double bond which cannot be optimized by the presence of the bulky methyl groups, in TDMAE. Third, the ground-state TDMAE dimers are assumed to have a binding energy of 0.1 eV, taking into account the presence of the $-N(CH_3)_2$ groups. Hence, a single 200 nm photon or a double-pump excitation at 266/800 nm will impart a $6.2 - 5.4 + 0.4 - 0.1 = 1.1$ eV excess energy to the $TDMAE_2^+$ dimer ion and an additional fraction of this to higher multimers $TDMAE_n^+$.

Of course the binding energy of 0.4 eV for $TDMAE_2^+$ and consequently the 1.1 eV excess energy imparted to this ion are nothing but educated guesses. Nevertheless the comparison between these two quantities is consistent with the observation of the evaporation of the multimers in the extraction chamber of the TOF-MS. In the femtosecond experiments, indeed, when the $TDMAE_2^+$ dimer ions evaporate a TDMAE moiety, it does so at times well within the residence time in the extraction region of the ions. This would be impossible without a total excess energy of 1.1 eV, substantially larger than the strength of the broken bond (0.4 eV). For this reason, the excess energy in $TDMAE_2^+$ (or larger in $TDMAE_{>2}^+$) is likely to be close to 1.1 eV. For convenience, this value is chosen in the following of the discussion, although an exact value of the excess energy is not essential for the interpretation of the data. This excess energy drives the subsequent reactive and nonreactive processes, each of which is discussed below.

IV.2. Competition between Stabilization and Evaporation Processes in the $(TDMAE)_n^+$ Cluster Ions. *IV.2.1. Stabilization of the $TDMAE_2^+$ Dimer Ion: Evidence for a Double Well in $TDMAE^+$.* In the 266/800 nm pump/probe experiments, when the dimer is likely to be the only dominant cluster species, an ion signal is observed at the mass of the $TDMAE_2^+$ dimer ion (400 amu). It presents a very short exponential decay time of 40 fs (see the 1.5 bar experiment at the bottom of Figure 4). This value is very surprising when compared to the 300 fs time constant of free TDMAE that we recalled in the Introduction. In that case, the initial wave packet propagates over the CI region from the valence configuration V of excited TDMAE to the zwitterionic configuration Z, an evolution that involves rapid deformations over several coordinates next to the central C−C bond of the TDMAE molecule.[6] We do not expect that the presence of a second TDMAE molecule next to a diradicaloid V excited state would so much accelerate the wave packet motion toward the conical intersection, for a 40 fs dynamics to be observed. The explanation we propose below results from the wave packet motion on the neutral surface, combined with dynamics in the ionic state of the dimer.

SCHEME 1: C-Centered $TDMAE^+$ Ion



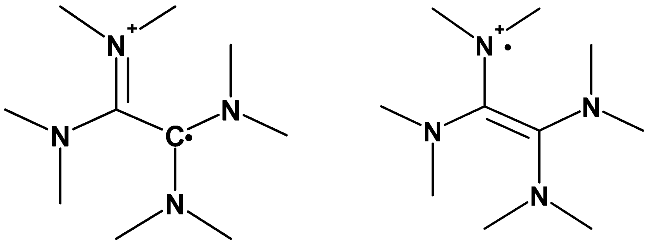
Structure I

The ionization of the dimer by the 266 + 800 nm two-pump sequence provides up to an ∼0.7 eV energy excess above the dissociation limit of the dimer ion as ground-state $TDMAE^+$ + TDMAE. When such excess energy is randomized over the vibration coordinates of the dimer ion, the latter is expected to dissociate as $TDMAE^+$ + TDMAE in the extraction region of the TOF mass spectrometer, where it resides for about 1μs. In that case, the dimer ion would not be detected at the $TDMAE_2^+$ mass (400 amu) but at that of $TDMAE^+$. Apparently, since a small ion signal is observed at 400 amu during a short time window of 40 fs, a channel is accessible at a short delay time between the two pump pulses, where the ∼0.7 eV excess energy is either taken by the ejected electron or stored in a metastable state of the ion moiety above the dissociation limit of the dimer ion. The first reason is very unlikely, since it is not consistent with photoelectron spectra that are currently under investigation in the free TDMAE molecule. Spectra taken with a single laser at 200 nm (same energy as in the present two-pump experiment 266+800 nm) yield negligible intensity for rapid electrons, most of the electron energies being close to 0 eV. A similar situation arises in these new experiments when the present two-pump scheme is used to sequentially ionize free TDMAE via the V configuration. Even in the case of a coupling of the V state with a Rydberg state, which is a likely situation, owing to the geometry differences of the ion with the initial ground-state neutral TDMAE, much energy will be retained as internal energy and not disposed in the electron kinetic energy. An electron that takes all the available energy is indeed emitted in a direct ionization process that leaves the ion with the geometry of the neutral molecule (the Franck−Condon geometry). Coming back to the dimer ionization, the above lines suggest that internal energy is retained in the ion moiety, probably sufficient for a subsequent dissociation of the dimer ion. For these reasons, we favor the alternative explanation made above that the observation of a dimer ion signal finds its origin in the presence of a metastable state in the $TDMAE^+$ moiety of the dimer ion. This question is substantiated now, following the ideas of a previous paper.[6]

IV.2.2. Considerations on the Low Electronic Configurations of $TDMAE^+$. Consider that excited TDMAE has the valence configuration V($\pi\pi^*$). Its ionization likely results from the ejection of the π^* electron out of the central C−C bond, hence preparing what we name the C-centered $TDMAE^+$ ion in Scheme 1 (structure I).

If the ionization proceeds from the zwitterionic configuration of TDMAE ($C^{+-}C^-$), the ejected electron would come from the negative carbon and the C-centered $TDMAE^+$ ion should be formed also. However, the C-centered ion is unlikely to be

SCHEME 2: N-Centered TDMAE$^+$ Ions



Structure II *Structure II bis*

the ground-state structure of TDMAE$^+$. Simply remember that the $\pi\pi^*$ transition absorption maximum lies at 6.5 eV in TDMAE,[4] i.e., above the known adiabatic ionization energy of TDMAE, 5.4 eV.[4] We surmise that the ground-state adiabatic configuration of the ion instead should have the nitrogen atoms bearing the charge. With one atom bearing the charge, ground-state TDMAE$^+$ should correspond to one of the following structures:

Structure II is the most likely. This stems from a comparison with recent calculations of Bouchoux et al. on vinylamine,[16] $NH_2CH{=}CH_2$. There, the most stable ion geometry is $NH_2^+{=}CH{-}CH_2^{\bullet}$. The radical site is on the terminal carbon, while the positive charge is delocalized over the NH_2^+ group and the central carbon atom. When transposed to TDMAE, this leads to structure II in Scheme 2. However the CH_3 groups of TDMAE are likely to accommodate the positive charge to a lesser extent than the hydrogen atoms in vinylamine. Hence, the positive charge in TDMAE$^+$ will essentially reside on a nitrogen atom. Importantly, the four nitrogen atoms of TDMAE are likely to play an important role in lowering the ionization potential to 5.4 eV (compared with vinylamine, 8.1 eV), through a delocalization of the positive charge over four equivalent mesomeric forms. The existence of an important charge delocalization over the nitrogen atoms in ground-state TDMAE$^+$ is confirmed by calculations in ref 17, which describes a totally and a partially delocalized form II of TDMAE$^+$ where the positive charge is carried, respectively, by the four $N(CH_3)_2$ groups or by two diametrically opposite ones.

The nitrogen atom that bears the charge in structure II is likely planar, as the nitrogen atom in vinylamine. In contrast, the four nitrogen atoms are likely pyramidal in structure I. Hence, the C-centered (structure I) and N-centered (structure II) forms of the TDMAE$^+$ ion are not likely to be resonant. Instead, structure II must be stabilized by resonance with respect to I, and both structures must be separated from each other by a barrier along the nitrogen pyramidalization coordinate that is called N-centered deformations in Figure 6.

The existence of two structures in the TDMAE$^+$ ion that are associated with two different electronic configurations could be confirmed experimentally by photoelectron spectroscopy in the event of a direct photoionization. Reference 6 has shown that ionization of the TDMAE molecule is mostly an indirect vibrational autoionization process. Nevertheless, a direct photoionization channel exists that is currently under investigation in the present laboratory. Preliminary photoelectron spectra obtained in a femtosecond pump−probe study of TDMAE seem to confirm the existence of such an excited state in the TDMAE$^+$ ion. Moreover, other experiments in our group have been performed on the TDMAE(Ar)$_{<10}$ clusters, with observation of the TDMAE$^+$(Ar) ion in the same two-pump experiment as here (266 nm + 800 nm). Again, an excited state of the TDMAE$^+$ ion is invoked to explain this observation [Chemical Physics Letters, submitted].

IV.2.3. Ionization of the TDMAE$_2$ Clusters, a Likely Scenario. As done several times in this paper, we assume that excitation (and now ionization) of a weakly coupled TDMAE subunit of a TDMAE$_2$ dimer proceeds in the cluster qualitatively as in the free molecule. Hence, the structures I and II of the TDMAE$^+$ ions are relevant to describe the ionization of TDMAE$_2$. They are simply lowered in energy by solvation.

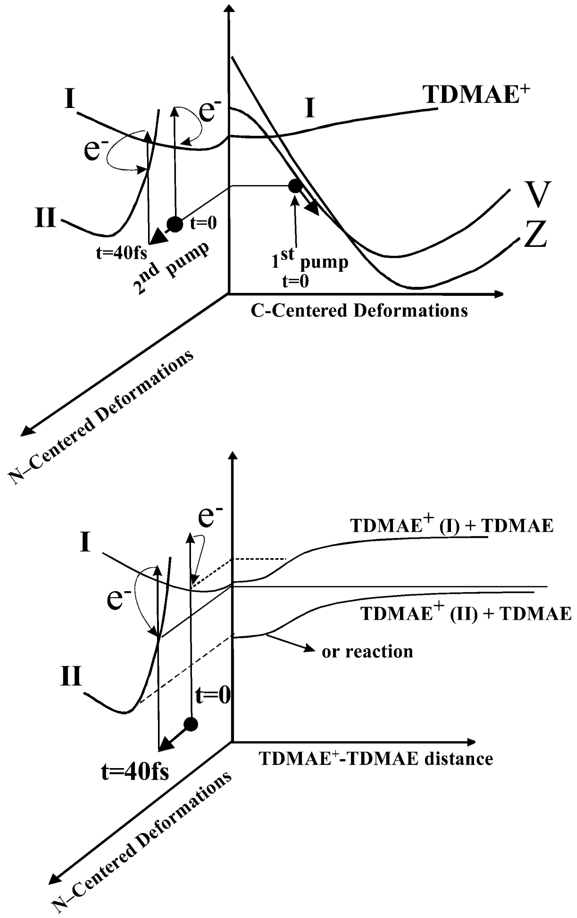


Figure 6. Schematic energy diagram of selected TDMAE, TDMAE$^+$, and TDMAE$_2^+$ potential energy surfaces. The top panel of figure shows cuts of TDMAE, TDMAE$^+$ surfaces along either the C-centered or N-centered deformation coordinates or along both of them. The following information is sketched: (i) Two potential surfaces (V and Z) of neutral TDMAE are shown as potential curves along the C-centered coordinate. We recall that this cordinate includes the CC-torsion and the C-pyramidalization deformations that define the conical intersection between the V and Z surfaces. (ii) The ion surface corresponding to structure I of TDMAE$^+$ (full curve labeled I) is shown as curves along the C- and N-centered deformation coordinates. (iii) Structure II of the TDMAE$^+$ ion is represented by the full curve labeled II along the N-centered coordinate. (iv) Excitation by the first pump laser is indicated by the vertical arrow labeled $t = 0$ above the C-centered deformation coordinate. The C-centered deformations that accompany the rapid V to Z evolution are shown as the → arrow starting at the top of the excitation arrow. The simultaneous N-centered deformations are schemed by the other → arrow starting at time $t = 0$. The two other vertical arrows that appear in the left part of this panel represent the ionization by the second pump laser, as the cluster is deforming along the N-centered coordinate. The curved arrows labeled e$^-$ indicate the maximum electron energy. The ionization brings the cluster to either ion form I ($t < 40$ fs) or II ($t > 40$ fs). The bottom panel is a transposition of these surfaces to the TDMAE$_2^+$ dimer ion. Cuts are drawn along the N-centered deformation of the TDMAE moiety and along the dissociation coordinate of the dimer ion. The notations are the same as those in the top panel.

We know from ref 6 and we transpose here in $TDMAE_2$ that the first pump laser at 266 nm communicates the valence configuration $V(\pi\pi^*)$ to a TDMAE subunit of the dimer. The second pump pulse ionizes the electronically excited subunit and should form the ion with structure I. When the delay between the two pump lasers is zero, the wave packet created by the first laser has not started to move and no deformation energy of the neutral is transported into the dimer ion. The dimer ion is formed with structure I and keeps this structure. It is conceivable that the two-pump scheme is favored in that case by the presence of a resonant Rydberg state of TDMAE that has a similar geometry as structure I of $TDMAE.^+$ At later times, the wave packet moves downward toward the conical intersection. This movement is schemed by the arrow above the “C-centred deformations” axis in the top sketch of Figure 6. It corresponds primarily to the torsion and pyramidalization about the central C atoms, but these “C-centred deformations” also induce “N-centered deformations” because they pull or push the amino groups and stimulate the depyramidalization of the N atoms. This was discussed in ref 18 when observing the umbrella oscillations of the dimethylamino groups. The movement creating these “N-centered deformations” is indicated by the other arrow in the top sketch of Figure 6 (that parallels the “N-centered deformations” axis). We shall note later in this paper that the Z state is stabilized by a second TDMAE molecule. This probably arises from partial charge transfer to an N-centered configuration as in the ion, thus exciting more strongly the “N-centered deformations”. The top sketch of Figure 6 suggests that rapidly, because of the N-centered deformation, the potential well I is no longer accessed by the delayed second pump laser or that enough impulse has been deposited along the “N-centered coordinate” for the barrier separating the ion structures I and II to be overcome. In both events, ionization proceeds toward form II of the ion, and up to 0.7 eV excess energy is deposited in the dimer ion as vibrational energy. This evolution stimulates either its dissociation as $TDMAE^+ +$ TDMAE or intracluster reaction (see section IV.4).

In contrast, we have seen that ionization during the first 40 fs gives an access to the structure I of the ion with almost no impulse along the “N-centered deformation” coordinates. Apparently the $TDMAE^+$ ion formed in that way does not react with the neutral nearby TDMAE molecule in the dimer. This is schematically described in the bottom scheme of Figure 6. According to this interpretation, the 40 fs decay observed for $TDMAE_2{}^+$ simply corresponds to an observation window to reach the metastable configuration I of the locally ionized $TDMAE^+$ moiety.

The potential well defining the metastable structure I of the $TDMAE^+$ ion is considered as “shallow” in the above discussion. This is substantiated now. The main argument is that a shallow well should trap only a small fraction of the $TDMAE^+$ dimer population. This stems from the small signal observed at mass 400 amu, at the lowest backing pressure, in the single-photon (200 nm) ionization experiment shown in Figure 2. Moreover, the peak at mass 200 amu in the same spectrum shows a shoulder typical of an evaporation process. The surface of the shoulder is greater than that of the mass peak at 400 amu. This suggests that the 400 amu signal corresponds to a small surviving fraction of the dimer ions. The energy at the bottom of the metastable well I in $TDMAE^+$ could be 6 eV, close to the vertical ionization energy of TDMAE[19] (this value could be lowered in the dimer). The ionization process, especially because it is dominantly an autoionization process, will disperse the ion energies over the accessible levels. The coldest ions, those that lead to the cluster ions observed at 400 amu, probably originate from a small fraction of direct ionization. Observing that stabilization at mass 400 amu is a minor channel, we infer that ΔE, the well depth of structure I, should be significantly smaller than $\Delta E'$, the energy excess between the ionization photon and the barrier separating structures I and II of the $TDMAE^+$ ion. This is schemed in Figure 7.

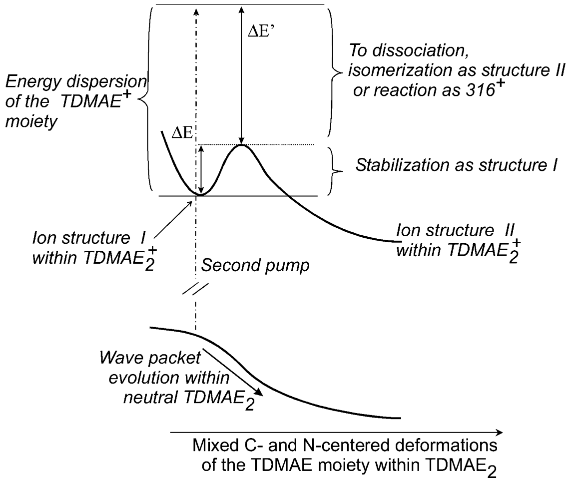


Figure 7. Energy scheme illustrating the energetics of the ionization. See the text for details (section IV.2.2).

IV.2.4. Evaporation in $TDMAE_{n>2}{}^+$ Multimer Ions: Evidence for Solvation Effects on the Relaxation Rate of Neutral Excited $TDMAE_n$ in the Valence State V. When the largest observed mass is the trimer, the same short 40 ± 10 fs dynamics is observed at the trimer ion mass. It can be interpreted as above in the dimer experiment. In particular, when the delay between the two pump laser is longer than 40 fs, the descending wave packet that is associated with the V−Z relaxation in the excited TDMAE moiety of the cluster is transferred on the dissociating side of the trimer ion. Hence the trimer dynamics will show up also at the mass of the dimer ion and at that of $TDMAE^+$ after a single or a double evaporation of neutral TDMAE. This is consistent with the observation in the middle panel of Figure 4 and gives a key to its interpretation. The temporal evolution at the mass of the dimer is the superposition of two contributions: (i) a monoexponential decay of 40 fs corresponding to the true excited dimer dynamics and (ii) another monoexponential time decay, 200 fs representing the V−Z relaxation in excited larger neutral clusters after evaporation of one or several neutral TDMAE subunits.

The 200 fs component assigned to the relaxation from the valence V to the zwitterionic Z configuration, is 100 fs shorter than the equivalent decay in the monomer (300 fs[6]). The diradicaloid V configuration should not be strongly affected in the trimer with respect to the monomer. In contrast, the zwitterionic configuration, with its charge separation character, should be more strongly solvated.[20] Hence the conical intersection between the V and Z configurations is readily moved at higher energies and thus is encountered at earlier times by the descending wave packet. This effect can be extended to all the multimers, as the same decay time constant 200 fs is observed for all multimers of larger than the dimer, as shown in the next section, through the observation of reaction products of the ionic dimer. This similar value for the V−Z relaxation time constant seems to imply that one or two TDMAE molecules are sufficient to stabilize the Z state in multimers. This is reasonable considering the TDMAE molecule with its eight methyl substituents is extremely bulky, and thus the addition of other units should impart little additional stabilization to the Z state.

At higher backing pressures of helium, 5 bar, the aggregation of the TDMAE becomes very important and the observation of a given multimer appears at all times dominated by the evaporation of higher multimers. This shows up as a single 200 fs time decay for all of the detected multimers. This is exemplified by the dimer ion signal shown in the top curve of Figure 4. At the same time, the decay measured at the mass of the monomer ion is dominated by the contributions of the fragmented multimers and its time constant decreases from 300 to 200 fs.

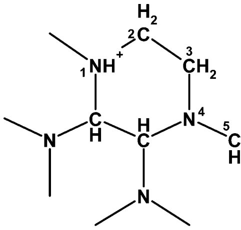
The time evolution measured at the multimer mass presents another difference in comparison with the behavior of the $TDMAE^+$ ion in the pump−probe study of free TDMAE.[6] The short-lived decay in the multimers is not followed by a long-lived evolution characterizing the detection of the excited TDMAE moiety when it has been relaxed to the Z configuration. Two explanations can be invoked. First, the detection of the low lying Z configuration in free TDMAE requires the absorption of a second 800 nm photon. This additional 1.5 eV energy increases the excess energy up to $1.1 + 1.5 = 2.6$ eV. This is enough to allow for complete evaporation of not too large cluster ions. In that case the long-lived evolution of the neutral cluster should show up at the $TDMAE^+$ mass. However, the large cluster present in the 5 bar experiment may not fully evaporate, and a long-lived evolution should be observed, even weakly at the dimer ion mass. This is not confirmed experimentally (see the top curve in Figure 4). This suggests that the successive evaporation processes that should eventually stabilize small multimer ions are dominated by another channel, the formation of ionic reaction products discussed in section IV.4.

IV.3. Multiphoton Ionization of Free TDMAE: Pathway to the 116 amu Ion. The results of the two-pump experiment on free TDMAE molecules, with the first pump at 200 nm and the second at 800 nm, are reported in section III.1. When the energy density of the 800 nm laser pulses is low, only 1 or 2 photons are absorbed. In that case, fragment ions of 45, 58, 88, and 102 amu are observed besides the parent ion at mass 200 amu. These ionization channels were observed and discussed in our former work.[6] At a higher energy density, the absorption of at least 2 or 3 probe photons disposes additional 3 or 4.5 eV excess energy in the $TDMAE^+$ ion and allows for the observation of the 116 and 73 amu ions. The decay time observed for mass 116^+ in Figure 1 is very fast, ∼20 fs, an indication that immediately upon deformation of neutral TDMAE out of the Franck−Condon region reached by the pump excitation at 200 nm multiphoton absorption of the probe photons can no longer create a precursor to mass 116^+. Hence, a geometry close to that of ground-state TDMAE seems to be important to access the precursor to mass 116^+. Apparently, the less constrained geometry that is reached after some delay between the two pump lasers leads to the formation of the ionic product at 73 amu but not to that of 116 amu.

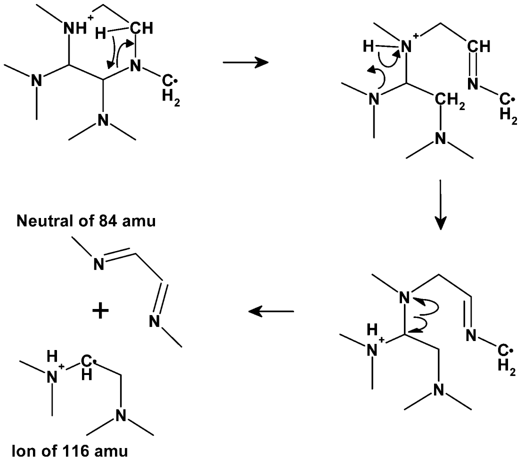
Two possible structures of the $TDMAE^+$ ion have been invoked in section IV.2.2, with the positive charge either carried by a central C-atom (structure I) or delocalized on the N-atoms (structure II). Structure I is accessed at zero time delay between the two pump lasers and might appear as a possible precursor of the ion mass 116 amu. This is unlikely, since this structure has no simple dissociation channel into the product of mass $116^+ + 84$ amu.

When it is considered that $TDMAE^+$ is a radical ion, a third distonic ion structure separating as much as possible the radical and the positive charge can also been invoked. Distonic ions are often more stable than their nondistonic isomers, but large energy barriers prevent the conversion from one form to the other.[21] Here, when the large excess energy provided by the multiphoton probe is considered, it is conceivable that the ionic precursor of the 116 amu ion is distonic. Several structures can be imagined. All of them result from one or several H-atoms shifts within the $TDMAE^+$ ion to put the positive charge and the radical in 1,4 or 1,5 positions. One of them could be cyclic according to Scheme 3.

SCHEME 3: Cyclic Distonic Form of the $TDMAE^+$ Ion



SCHEME 4: Possible Dissociation of the Cyclic Distonic Ion of Structure III and Formation of an Ion of 116 amu



It was chosen for the following dynamical reason. The access to the precursor of the 116 amu ion is favored by a geometry close to that of ground-state TDMAE: a planar N_2CCN_2 skeleton, pyramidal N-atoms, and the dimethyl amino groups disposed like a propeller for steric reasons. Such a geometry, which puts the methyl groups in good position to stimulate the cyclization, could be close to that of the transition state that enables the H-atom shifts, thus opening the route to structure III. Conversely, at short nonzero delays between the two-pump pulses, the torsion about the central CC bond would be sufficient to put the neutral molecule quite far from the planar geometry. Hence, the ionization pulse would create $TDMAE^+$ quite far from the transition state that gives access to structure III, and the subsequent evolution would be different from that discussed below for structure III.

It has already been said that structure III is formed with a large excess energy because its formation is multiphotonic. Its subsequent fragmentation is likely. A possibility is the elimination of the neutral moiety of 84 amu together with the formation of the 116^+ ion. A tentative series of H-atom shifts that ends up with the dissociation of the 200^+ ion into $84 + 116^+$ is shown in Scheme 4.We note that, in the extraction region of the mass spectrometer, the formation of structure III should be the limiting step to complete this series of transformations in less that 1 μs.

IV.4. Reactions in $TDMAE_n^+$ Cluster Ions. The dominant ionic reaction channel in $TDMAE_n^+$ multimer ions is the formation of ions of general formula $(116)_m(200)_p^+$. We recall that this writing is simply a convenience to point out that the mass of these ions is $m \times 116 + p \times 200$. It does not anticipate a structure where neutral TDMAE molecules of 200 amu could be recognized.

The $(116)_m(200)_p^+$ ions originate from TDMAE clusters that have absorbed a single photon of the second pump laser. Hence, the maximum excess energy carried by the ionic precursor to these ions is about 1.1 eV when the precursor is the dimer ion and slightly larger in a larger cluster (see section IV.1). We first examine the dynamics of the reaction forming the $(116)_m(200)_p^+$ ions to establish that these ions are actually formed by an intracluster ion−molecule reaction as anticipated from the beginning of the present paper. We also discuss what the time scale of this reaction could be (section IV.4.1). After these general considerations, we discuss more specifically the dynamics of the reaction in the dimer ion (section IV.4.2) and in larger clusters (section IV.4.3). We also show that the observation of the reactive products carries information on the dynamics of the neutral excited cluster (section IV.4.4). Finally we propose, quite tentatively, a formation mechanism and a structure to the $(116)(200)^+ = 316$ amu ion (section IV.4.5).

IV.4.1. General Considerations on the Dynamics of Reactions Forming the $(116)_m(200)_p^+$ Ions. We anticipate from the beginning of the present paper that the $(116)_m(200)_p^+$ ions are produced in an ion−molecule reaction within $TDMAE_n^+$ clusters and not by ionization of a product formed by reaction in the excited neutral cluster. This stems from the following arguments, taking the product of mass 316 amu as an example: First, it is observed with no rise time while varying the delay between the two pump photons. This implies that the reaction actually proceeds in the ionic state, not on the intermediate neutral state; otherwise a rise time should be observed corresponding to the formation of an hypothetical neutral precursor to mass 316. Second, the rapid transient measured at mass 316 amu in Figure 5 is fitted by the same decay time, $\tau_A = 200$ fs, as that corresponding to the V−Z relaxation time in the multimers (see the discussion in section IV.2.4). This is the signature that the second pump activates a multimer precursor to mass 316^+. Hence mass 316^+ originates from an intracluster reaction within TDMAE $_n^+$ cluster ions.

The present experiment does not provide a direct access to the time constant for reaction within cluster ions, since the latter proceeds in the ionization chamber of the mass spectrometer, after the second pump pulse has been absorbed by neutral $TDMAE_n$. However, several observations that are discussed below suggest that the reaction rate forming the ion of mass 316 amu within $TDMAE_2^+$ has about the same rate as the fragmentation of $TDMAE_2^+$ as $TDMAE^+ + TDMAE$.

Consider the bottom panel of Figure 2 that reports the 200 nm ionization of $TDMAE_{\approx 2}$ clusters. The same 1.1 eV excess energy as that in the 266 + 800 nm two-pump experiment is deposited in the cluster. It appears that the peak at mass 316^+ is much more intense than the peak at mass 400^+ and has a surface equivalent to the shoulder in the 200^+ peak that has been assigned to the evaporation of a neutral monomer from the dimer ion in section IV.2.2. This suggests that when the 1.1 eV excess energy is disposed in the dimer ions, reaction and fragmentation compete with approximately equal efficiencies.

Turning now to the two-pump experiment, it appears from section III.4.1 that the time evolution measured at the $TDMAE^+$ mass has the same rapid transient of 200 fs as that measured with multimers. This suggests that the evaporation process allowing detection of the small multimer ions detected at the mass of $TDMAE^+$ is not fully overcome by reactive processes forming ions at mass 316^+. In turn the large intensity of the 316 amu peak indicates that reaction is not a minor process and equivalent rates for both evaporation and reaction seems consistent with the present observation.

If we consider now that the evaporation of $TDMAE_2^+$ as $TDAME^+ + TDMAE$ is a statistical process, we can estimate that its time constant lies in the 10 to 100 ns range, owing to the 108 vibrational modes of $TDMAE^+$ and the 0.7 eV excess energy over the dissociation. This is also the order of magnitude of the reaction time within the dimer ions.

IV.4.2. Dynamics of the Intradimer Ion Reaction. We anticipate that the reaction forming the ionic compound of 316 amu occurs after energy has been released from the Franck−Condon region of the ionized dimer to a form where the ionized moiety of the dimer ion has the structure II. This stems from two considerations. First, no contribution of 40 fs kinetics is found at mass 316 either as a rise time or as a decay. Second, when the dimer is blocked in the metastable well I, it cannot dissociate or react, else it would not appear at mass 400. These two considerations do not conflict because trapping in well I is a minor channel under our experimental conditions, as discussed in section IV.2.2.

The time evolution of mass 316 has the same 200 fs dynamics (see Figure 5) as the full V to Z relaxation that was discussed in section IV.2.4. This suggests that provided the dimer ion has passed the barrier separating forms I and II, no higher barrier appears along the ionic reaction path. Such a barrier would indeed generate an observation window for the reaction, and the observation dynamics of mass 316^+ would not be 200 fs. Nevertheless, a smaller barrier is present along this reaction path. Its existence stems the FT-ICR experiments where $TDMAE^+$−TDMAE collisions at thermal energy were unable to activate the formation of any reaction product. In these experiments indeed, the $TDMAE^+$ ion, which has been collided many times, is believed to be stabilized in its stable form II. We are left with two limits for this barrier; it cannot be overcome at thermal energy for collisions of thermalized $TDMAE^+$, but it is lower than the energy barrier separating forms I and II of the dimer ion.

IV.4.3. Reaction Dynamics in Larger Cluster Ions, Formation of the $(116)_m(200)_p^+$ Products. At higher backing pressures in the molecular beam, larger multimers than the dimer are created in the expansion. Evaporation and ion/molecule reactions certainly take place in these large systems in a way that is comparable to the evolution of dimers where a neutral fragment of 84 amu is eliminated. Hence, products of general formula $(116)_m(200)_p^+$ are expected in large clusters, since the presence of many TDMAE units allows for several of these reactive processes to be active steps sequentially, in competition with evaporation processes. Such a chain of reactions is limited by the size of the initial cluster, the available excess energy, and the time spent by the clusters in the extraction chamber of the TOF-MS (about 1 μs). More specifically, in Figures 2 and 3, the products of the following masses have been observed: 516^+ resulting from the elimination of one neutral 84 amu residues, 432^+ due to the elimination of two neutral 84 amu residues, and 548^+ from the elimination of three residues.

The temporal behavior is the same for each ion/molecule product and is close to that observed at mass 316 amu in Figure 5: a 200 fs monoexponential decay followed by a plateau. The decay corresponds to the relaxation from the valence state V to the zwitterionic state Z of the locally excited neutral TDMAE within the multimer parent. Evaporation within the neutral clusters does not seem to have influenced these decays since no population growth has been observed in any species at long delays (100 ps), in accordance with simple RRKM evaluations which place the time scales of these events in the nanosecond range, far beyond the time scale of the V−Z relaxation. Hence, the observed mass distributions of the cluster products simply reflect the competition between the possible evaporation and reaction channels in the ion.

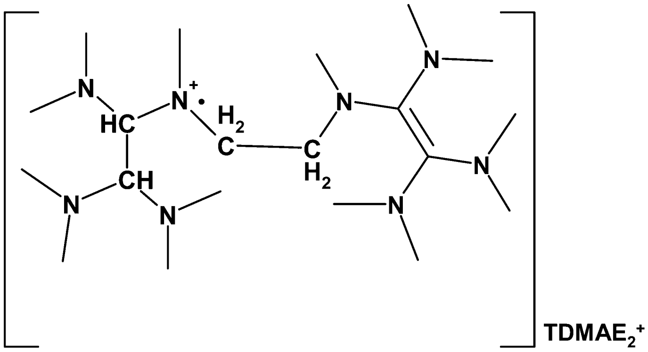
Such a competition between evaporation and reaction has already been reported in vinyl chloride ionic clusters where the reaction in large multimers was quickly terminated by evaporation.[22] However this reaction is driven by the rather simple elimination of HCl with a minimum of reorganization. In our case the necessary steps for reaction are more complex and need to be detailed. This is the subject of section IV.4.5 below.

IV.4.4. Ionic Reaction Products As Probes of the Z State Relaxation in the Neutral Cluster. The observation of a long decay (> 500 ps) in neutral multimers arises, as we already noted, from the slow decay time of the Z state in neutral TDMAE clusters. This delay is much longer than the equivalent one found in free TDMAE molecules, 100 ps.[6] This is the sign of a profound modification of the decay characteristics of the Z to the charge transfer state in the cluster environment. When the excited TDMAE$_n$ multimer reaches the Z state, it is far from the Franck−Condon region corresponding to local excitation of a TDMAE moiety by the first pump laser. The present, longer lifetime of the Z state indicates that it is certainly excessive to consider the excitation as local in this distant region. Most likely, a quasi complete charge transfer in the Z state due to the presence of solvating TDMAE molecules can be inferred, which also simulates the motion along the N-centered coordinates (section IV.2.3).

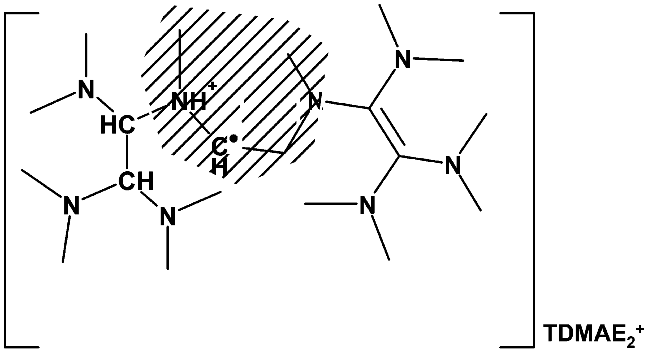
IV.4.5. Possible Formation and Structure of the 316 amu Ions. The discussion now focuses on the formation of the 316 amu ion. At a first glance, we could simply consider that mass 316 originates from mass 116 by addition of a monomer. In that case, the reactive mechanism would be that discussed in IV.3. This is very unlikely however, since formation of the 116 amu ion needs a high intensity of the second pump to reach the highly constrained distonic ion III shown in Scheme 3. This would evaporate the resulting cluster. Instead, the formation of the 316 amu ions does not require a large energy of the second pump laser to be observed. Moreover this ion can be observed when ionizing the TDMAE dimer by a single 200 nm photon that provides the dimer with the same energy as the 266 + 800 nm two-pump ionization scheme. Hence, a single 800 nm photon is likely to induce the formation of the 316 amu ions in the present experiment, with no more than 1.1 eV excess energy in the dimer ion. Additionally, the constrained geometry corresponding to short delays between the two-pump laser pulses is not suggested by the time dependence of the 316 amu ion signal in Figure 5: a $\tau_A = 200$ fs decay is observed here, much larger than the extremely short one observed in Figure 1 for mass 116. We do not expect that solvation of TDMAE by a single TDMAE molecule could so much relax the requirements for the formation of the distonic structure III in the TDMAE$^+$ moiety of TDMAE$_2$.

It has been discussed already in section IV.4.2 that the reaction forming the 316 amu ions proceeds from structure II of the TDMAE$^+$ moiety within the TDMAE$_2^+$ dimer ion. As a result, clues to the reaction mechanism within the TDMAE$_2^+$ ion can be provided by the reaction mechanism of the vinylamine ion with an alkene as studied by Bouchoux et al.[16] H-atom transfer is the driving force for the reaction. When transposed to TDMAE$_2^+$, a reaction path involving a series of three such H-atom shifts could lead to the formation of a bond between the two moieties of the TDMAE$_2^+$ dimer, as in Scheme 5.

SCHEME 5: Possible Nondistonic Precursor of the TDMAE$_2^+$ Intracluster Reactions



SCHEME 6: Possible Distonic Precursor of the TDMAE$_2^+$ Intracluster Reactions



Again, the excess energy contained in this ion is large, and it can evolve toward a distonic structure where H$^+$ will be almost free to migrate on any nitrogen atom within the ion. The shaded area in Scheme 6 is, after migration of the H$^+$ ion, the precursor of the group at 84 uma that is likely to leave after two further H-atom transfers. In that case, the TDMAE$_2^+$ ion would dissociate as 84 + (159 + 157)$^+$, thus forming the desired 316$^+$ ion.

Of course, the proposed reaction path is very hypothetical and certainly not unique, although we have been surprised by the paucity of reaction products. Many competing reaction schemes would be certainly manifest if many reaction paths were present. An alternative reaction path, very different in origin from the one above, could involve the formation of N−N bonds and the elimination of tetramethylethylene $(CH_3)_2C{=}C(CH_3)_2$ (mass 84 amu). This is inspired by reactions in ammonia cluster ions by Huisken and Färber[23] leading to H_2 elimination and formation of solvated hydrazine ions. There, the driving mechanism is proton transfer instead of H-atom transfer, a process made energetically accessible by the large energy disposed in the ammonia cluster, 8.8 eV.[24] Such an energy reservoir is not available here with terminal methyl groups on the nitrogen atoms in TDMAE$^+$. This reinforces a mechanism grounded of the initial H-atom transfer, as that proposed above.

The reactions in higher clusters are certainly even more complex and involve a multiplication of the previous reactions. However, changes due to increased solvation are expected, one of the most important being the energetics. For example, when the dimer and the trimer ions are compared, solvation of TDMAE$^+$ by a second TDMAE molecule in the trimer ion likely increases by ca. 0.4 eV the excess energy deposited by the pump photons. This could increase the possibility of bond rearrangements within the cluster ion.

V. Summary and Conclusions

The dynamics of tetrakis(dimethylamino)ethylene, TDMAE, and of its clusters TDMAE$_n$ have been observed in the neutral excited valence state and in the ionic state, in light of the monomer dynamics, studied in a previous paper.[6]

The early dynamics of neutral multimers corresponds to a valence-to-zwitterionic switch of the excited electronic configuration at a conical intersection. It appears faster in the multimer environment, 200 fs versus 300 fs in free TDMAE. This could be interpreted through the solvation of the Z state, crossing the valence state earlier and making the access to the conical intersection quicker. This effect is already present with a single solvating molecule.

The central part of the work concerns the ionic dynamics of both TDMAE$^+$ and TDMAE$_n$$^+$. A sequential excitation by two femtosecond laser pulses, using the V or Z neutral state as a relay, has allowed various regions of the ion potential surfaces to be reached. Exploring the resulting processes, evaporation and chemical reactions, as a function of the time delay between the laser pulses has helped to resolve several issues on the reactivity of the ionic monomer and multimers.

The present work suggests the existence of a metastable form to the TDMAE$^+$ ion, with initial location of the positive charge on the central carbon, while the stable TDMAE$^+$ ion should delocalize the charge on the nitrogen atoms. The existence of metastable TDMAE$^+$ was inferred to account for a small fraction of the TDMAE$_2$ dimers that survive as the TDMAE$_2$$^+$ dimer ion in the ionization chamber of the mass spectrometer at short delays between the two pump laser pulses. Moreover, when trapped in the metastable potential well, the TDMAE$^+$ ion seems to be nonreactive with the neutral TDMAE moiety of TDMAE$_2$$^+$. In contrast, at a larger delay between the two pump lasers, the TDMAE$_n$$^+$ cluster ions are formed beyond the barrier that prevent the exchange between both isomers of the TDMAE$^+$ moiety. In that case, TDMAE$_n$$^+$ cluster ions follow one or both behaviors: evaporation of neutral TDMAE or attack of neutral molecules to form reaction products of general formula TDMAE$_n$(116)$_m$$^+$. In that sense, the two-pump laser excitation, with the proper delay between the pumps, has been able to tune the reactivity of the TDMAE$^+$ moiety.

In the dimer ion, the product at mass 316$^+$ seems to be the major ionic outcome of the reaction. This reaction has been shown to compete with the evaporation of neutral TDMAE. The comparison of the reaction induced in a TDMAE$_2$$^+$ dimer with a TDMAE$^+$ + TDMAE collision experiment in an FT-ICR setup implies that a barrier to the ion molecule reaction exists but is lower than 1.1 eV. In multimers, the reaction results in the successive elimination of mass 84 amu residues and efficiently competes with the natural evaporation in clusters occurring with the substantial energy imparted to the cluster (>1 eV). We have tentatively assigned these reaction products and proposed a mechanism for the reaction, inspired by the reaction mechanisms of a similar ion, the vinylamine ion.[16]

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