Consecutive photodissociation of a single complex molecular ion

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Using the positively charged aniline ion $(C_6H_5NH_2^+)$ as a test molecule, we demonstrate that it is possible to study consecutive photodissociation of complex molecular ions at the single molecule level in an ion trap. When a single $C_6H_5NH_2^+$ ion is exposed to laser light at 397 nm and 294 nm, direct or consecutive photodissociation leads to the production of a range of smaller polyatomic molecular ions such as $C_5H_6^+$ and $C_3H_3^+$. The applied method is very versatile and can, e.g., be used in combination with free electron lasers or synchrotron radiation sources.

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Photodissociation is a general tool for gaining information about the structure and dynamics of molecules [1], and it is known to play an important role for the physics and chemistry of, e.g., planetary atmospheres [2] and in interstellar clouds [3]. Photodissociation can also be a pathway to create otherwise not easily accessible neutral molecules [4,5] in the gas phase. Furthermore, some specific molecular anions [6] and various positively charged radicals [7] have been produced very efficiently through photodissociation. In general, for charged photofragments, both the absolute number of ions produced as well as the chemical composition of the charged fragments can efficiently be determined by the use of time-of-flight (TOF) [8,9], quadrupole [8,10], or cyclotron [11,12] mass spectrometers. However, for complex molecular ions which often disintegrate into smaller fragments through a series of consecutive dissociation steps when exposed to light, the use of the above mass spectrometers makes it difficult to identify the individual steps in the photodissociation chains since experiments typically involve larger ensembles of ions [13,14]. If only a single ion is present in the experiment at the time, and its composition can be determined nondestructively at various times, one will avoid this problem. Recently, we demonstrated a technique, based on rf excitation of center-of-mass resonant modes, that allows nondestructive identification of a single molecular ion trapped and sympathetically cooled by a laser-cooled atomic ion [15]. Besides allowing for consecutive measurements of the molecular ion mass with a relative mass resolution of better than 10⁻³ during an experiment, the sympathetic cooling leaves the molecular ion translationally very cold $(\approx 10 \text{ mK})$ and spatially localized to better than a few microns [15].

In this Rapid Communication, we describe how our method can be used to study the consecutive photodissociation of a single complex molecular ion. Using the aniline ion irradiated by the combination of cw light at 397 nm and nanosecond pulsed light at 294 nm as an example, we show how the sequential breakage into lighter fragments can be monitored nondestructively on time scales up to several minutes, and potentially up to several hours. Among the variety of ions produced and identified, the lightest species, robust against further photodissociation, is found to be $c-C_3H_3^+$ (cyclopropenylium).

Our motivation for the present study is manifold. First, we want to prove that our nondestructive detection method of a single trapped molecular ion allows detailed studies of the time evolution of light-induced consecutive fragmentation at time scales from milliseconds up to several hours, a time span unmatched by other techniques. Second, we want to prove that the non-destructive detection technique of consecutive fragmentation is a viable way for probabilistic preparation of a wealth of single molecular ions which could be used as targets for, e.g., astrophysical studies. Third, more generally we want to prove that studies of spatially localized and very cold single ions can be extended from atomic and diatomic systems [15] to complex molecular systems. This opens new opportunities in molecular science, including molecular rotational dynamics and chemical reaction dynamics on ultralong time scales.

Our experimental setup is sketched in Fig. 1. The central part of the experiments is a linear Paul trap consisting of four rods, each divided into three sections. By keeping the central section of each rod at a lower voltage than the end sections, confinement of positively charged ions along the trap axis



FIG. 1. (Color online) Sketch of the experimental setup.

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FIG. 2. CCD images of a laser-cooled ${}^{40}Ca^+$ ion. (a) A single ${}^{40}Ca^+$ ion is trapped. (b) One ${}^{40}Ca^+$ ion and one nonfluorescing molecular ion. Notice the displacement of the ${}^{40}Ca^+$ ion due to the Coulomb interaction between the two trapped ions. (c) As (b), but with the center-of-mass mode of the two-ion system resonantly excited. The fluorescence from the ${}^{40}Ca^+$ ion appears axially smeared out due to the long CCD exposure time. The white scale bar in all three images corresponds to 25 μ m.

(the z axis) can be achieved. Confinement in the radial plane (xy plane) is achieved by a time varying two-dimensional quadrupole field created by applying radio frequency (rf) voltages with opposite signs with respect to the nearest rods. Details about the trap parameters can be found in Ref. [16].

Before loading the molecular ion of interest, we first load a single ⁴⁰Ca⁺ ion into the trap [17]. This ion is Doppler laser cooled on the 4s ${}^{2}S_{1/2}$ -4p ${}^{2}P_{1/2}$ transition by sending counterpropagating 397 nm light beams ($I \approx 0.1 \text{ W/cm}^{2}$) along the trap axis as well as by having a single 397 nm laser beam ($I \approx 0.02 \text{ W/cm}^{2}$) in the radial plane (see Fig. 1). To avoid optical pumping into the $3d {}^{2}D_{3/2}$ level, a single 866 nm repumping beam is sent in along the trap axis. As seen in Fig. 2, the scattered cooling light at 397 nm can be used to create an image of a single ⁴⁰Ca⁺ ion at the charge-coupled device (CCD) chip of a camera system(magnification ≈ 15) when the ion is sufficiently cold ($\approx 1-10 \text{ mK}$).

Next, a gas of aniline is leaked into the vacuum chamber at a pressure of $\approx 10^{-9}$ mbar, which is about an order of magnitude higher than the background pressure in the trap region. A pulsed laser beam ($\lambda \approx 294$ nm, duration=5 ns [full width at half maximum (FWHM)], rep. rate=20 Hz, $I_{Peak} \approx 10^7 \text{ W/cm}^2$) is focused to a spot size of $\approx 100 \ \mu\text{m}$ in the center of the trap to produce a single $C_6H_5NH_2^+$ ion through resonantly enhanced two-photon ionization (R2PI) via the $S_0 \rightarrow S_1 0_0^0$ transition [18]. After ≈ 10 s of sympathetic cooling, the nonfluorescing molecular ion becomes part of a two-ion Coulomb crystal. This is observed indirectly through the change in the position of the fluorescing ⁴⁰Ca⁺ ion in the camera images (see Fig. 2). At this stage, the 294 nm photoionizing laser is shut off, but the cooling laser beams remain present. A repeated series of nondestructive mass scans is initiated around the masses expected to be produced in photodissociation of the positively charged aniline ion by the pulsed ionization light (294 nm) or the continuously present cooling light (397 nm). In each mass scan, the frequency of a small sinusoidally varying voltage applied to the end sections of two trap rods (see Fig. 1) is swept across the centerof-mass mode resonance of the two-ion system. With the trap voltages applied, the resonance frequencies are typically in the range 50-100 kHz. In Fig. 2(c), one clearly observes how the resonantly excited motion of the two-ion system results in an axial smearing of the fluorescence from the 40 Ca⁺ ion on the CCD camera when it is exposed for 0.1 s. As discussed in detail in Ref. [15], the mass of the nonfluorescent ion can now be deduced from the measured resonance frequency. The jump time between masses is cur-

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FIG. 3. (Color online) (a) Molecular ion mass spectrum. The height of the bars indicates how often a specific ion mass was detected in a series of experiments. (b) Three recorded time sequences of the photodissociation of $C_5H_6^+$ by a single 397 nm photon.

rently limited to 0.1 s by the fluorescence light collection efficiency of the imaging lens system, but the technique can rather simply be improved to become an order of magnitude faster.

In Fig. 3(a), the frequency at which a specific molecular ion mass has been detected during a series of 77 experiments is presented. In contrast to previously reported experiments on R2PI of aniline using light in the same wavelength range as here [19-21], the mass spectrum presented in Fig. 3 contains a very low amount of C₆H₅NH₂⁺ ions. In fact, the C₆H₅NH₂⁺ ion peak was by far the highest in previous experiments [19–21]. The main reason for this difference lies in the possibility in our experiments for consecutive photodissociation of a newly formed C₆H₅NH₂⁺ ion by absorption of a photon from either the 397 nm beams or from the 294 nm beam before the latter is turned off. In the time span (≈ 10 s), from a single C₆H₅NH₂⁺ ion is produced to a molecular ion is sympathetically cooled and detected, the $C_6H_5NH_2^+$ ion was actually exposed to ≈ 200 pulses of 294 nm laser light.

As can be seen from Fig. 4, which shows the ground state energies of the most abundant photofragments in the experiments together with the indication of possible single (two) photon dissociation (ionization) processes, the presence of the 294 nm laser light can lead to formation of a $C_5H_6^+$ or a lighter mass ion through dissociation even when the $C_6H_5NH_2^+$ ion is formed in the vibrational ground state. With the $\approx 10^7$ W/cm² peak intensity of the 294 nm pulses, we expect from previously reported photoionization experiments that the probability of photofragmentation should be a few percent per pulse [21,22]. Furthermore, the $C_6H_5NH_2^+$ ion is not necessarily left in the vibrational ground state when produced through R2PI using light at 294 nm. Indeed,



FIG. 4. (Color online) Energy level scheme with indication of the ground state energies of several relevant molecular ions relative to the ground state of neutral aniline. The dashed (solid) arrows indicate some of the photodissociation paths observed in the experiments due to the presence of light at 294 nm (397 nm). (The lengths of the arrows correspond to photon energies.)

supplementing measurements of the R2PI process, employing photoelectron spectroscopy and a supersonic molecular beam, showed that with the same pulsed laser tuned to 294 nm, more than 60% of the ions will be produced in a vibrational state from where formation of a $C_5H_6^+$ ion is energetically allowed through absorption of a single 397 nm photon [23]. For a room temperature aniline gas as used in the present trap experiments, the fraction of vibrationally excited $C_6H_5NH_2^+$ ions may be even higher.

However, a $C_6H_5NH_2^+$ ion formed in the ground state cannot be dissociated by a single 397 nm photon. Hence, in some rare cases we do observe a single $C_6H_5NH_2^+$ ion surviving not only the initial ionization and sympathetic cooling phase (≈ 10 s) but also a very long time interval (>100 s) with the 397 nm cw light present.

In the phase of the experiment where only the 397 nm light is present, single or consecutive photofragmentations are often observed. While examples of observed single-step photodisociation of $C_5H_6^+$ are presented in Fig. 3(b), in Fig. 5 an event where the three ions $C_5H_6^+$, $C_5H_5^+$, and $C_3H_3^+$ were consecutively produced from the parent aniline ion is presented. That the latter stepwise photofragmentation should be energetically possible through consecutive absorption of single 397 nm photons is obvious from Fig. 4. In several experiments we detected, however, only a $C_5H_6^+$ ion followed by a $C_3H_3^+$ ion. It may be that in such experiments a $C_5H_5^+$ ion was formed but not detected before further photofragmentation. Yet in other experiments single $C_5H_6^+$ or $C_5H_5^+$ ions have been observed to be rather stable against photodissociation by 397 nm light (lifetime: >100 s).

The most stable photofragment ion produced is the $C_3H_3^+$ ion which was never observed to photodissociate due to the 397 nm light over time scales of ≈ 1000 s. The $C_3H_3^+$ ion is known to exist in two possible low-energy isomers: The ground state cyclic molecule, cyclopropenylium, and a much



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FIG. 5. (Color online) A consecutive photodissociation sequence observed in an experiment. The dashed (solid) wriggly arrows represent 294 nm (397 nm) photons responsible for the fragmentations.

more reactive and slightly excited linear molecule, propagylium [24]. In order to determine if the structure of $C_3H_3^+$ is either "linear" or cyclic, we performed a series of experiments where the $C_3H_3^+$ ions were exposed to C_2D_2 molecules at a partial pressure of $\approx 10^{-8}$ torr. The "linear" configuration has a high cross section for substitution reactions leading to the formation of $C_3H_2D^+$ or $C_3HD_2^+$ [25]. Since none of these ions were detected in a total reaction time of ≈ 5000 s distributed over 10 trials, we conclude that essentially only the cyclic c- $C_3H_3^+$ ions are formed.

The above results imply that with a vapor of neutral aniline as the starting point, any of the ions $C_6H_5NH_2^+$, $C_5H_6^+$, $C_5H_5^+$, and $c-C_3H_3^+$ can be prepared in a probabilistic but certain way. These as well as other produced and identified single ions may in the future be the starting point for reaction studies or photofragmentation experiments of relevance for, e.g., astrochemistry [26], using not only lasers as light sources but also free electron lasers and synchrotron radiation. For singly charged molecular ions larger than the ones considered here, e.g., protonated biomolecules, the charge is expected to have negligible effect on the photodissociation dynamics. Studies employing the technique presented here may then provide important information on similar processes in the corresponding neutral molecules. To circumvent the problem of photofragmentation by the laser cooling light, one would either have to spatially address only the atomic coolant ion by, e.g., introducing a single tightly focused cooling laser beam propagating at a 45° angle with respect to the trap axis or alternatively apply a laser cooling scheme involving only red and infrared light as recently demonstrated [27].

The applied method of nondestructive ion identification can be used both to study very slow photofragmentation processes under continuous light exposure and to investigate stepwise photodissociation of molecular ions when exposed to a series of laser pulses. Complementarily, the single ion identification technique could also be used to monitor the buildup of complex molecules through consecutive reaction processes. While the mass resolution, typically $\frac{\Delta m}{m} \approx 10^{-3}$, cannot compete with the best methods known today [28], it is more than an order of magnitude better than similar methods based on larger cold ion ensembles [29,30].

In conclusion, it has been demonstrated that it is possible to study consecutive photodissociation of a single complex molecule as well as to probabilistically prepare a specific single molecular ion through photofragmentation. The experimental arrangement easily allows for the introduction of light from a large variety of advanced light sources.

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