Direct observation of a photochemical activation energy: a case study of acetone photodissociation

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Abstract
The ability to observe and quantify the conversion of electronic potential energy to vibrational kinetic energy in a molecule after photoexcitation is essential to understand and control the outcome of photoinduced molecular fragmentation. We exploit the high selectivity of photoelectron–photoion coincidence detection to distinguish different relaxation channels and observe the fragmentation behavior of each channel. We demonstrate the concept by investigating the fragmentation of gas-phase acetone molecules initiated by three-photon excitation to high lying Rydberg states between 9.0 and 9.5 eV above the ground state. By applying variations of the photon energy, pulse duration (100–200 fs) and pulse energy, we are able to fully characterize the fragmentation process. Rydberg states between 5s and 8s are populated, which undergo ultrafast internal conversion to lower states. The corresponding non-adiabatic dynamics in the neutral molecule cause the conversion of electronic to vibrational energy, leading to fragmentation. Our scheme allows us to directly measure the activation energy for fragmentation of acetone to an acetyl ion and a methyl radical, which we determine to be \((0.79 \pm 0.04)\) eV. Longer laser pulses result in an increased fragment-to-parent ratio, representing a higher probability for relaxation because the relaxation time constants are comparable to the pulse duration. Upon excitation to Rydberg states at 9.5 eV we surprisingly observe reduced fragmentation, although \(\sim 2\) eV are coupled into vibrational energy, indicating that different relaxation pathways become active, which results in a change of the redistribution of vibrational energy within the molecule. Fragmentation due to subsequent excitation of the cation is found to play a minor role.

Keywords: nonadiabatic dynamics, photoelectron–photoion coincidence, photodissociation, acetone

(Some figures may appear in colour only in the online journal)

Introduction

Photoinduced fragmentation of molecules can be caused by different mechanisms. For example, ionization to different cationic states yields different ion fragments because different electrons (HOMO, HOMO-1, …) are taken from the molecule [1, 2]. If excited states of the neutral molecule are involved in the ionization process, internal conversion (IC) can occur and strongly influence which cationic states are accessed [3, 4]. IC is accompanied by nonadiabatic coupling of electronic and nuclear degrees of freedom and thereby facilitates the conversion of electronic to vibrational energy. In this case, even
ionization to the ionic ground state can lead to fragmentation because energy is coupled into vibrational modes of the molecule. This vibrational energy is first concentrated in one or few modes and will subsequently be distributed to other modes by intramolecular vibrational energy redistribution, causing the breakage of chemical bonds. The amount of energy that is coupled to vibrations during the IC relaxation process can directly be obtained from photoelectron (PE) spectra by considering the photoexcitation energy and the kinetic energy of the PE. The minimum energy that must be supplied to the molecule in order to cause fragmentation is the activation energy. By recording separate PE spectra for the parent and fragment ions, which is achieved by coincidence detection of PEs and photoions, this activation energy can be determined directly from the experiment with high accuracy.

Photoinduced fragmentation of acetone is one of the most comprehensively studied photochemical reactions [5]. The highest occupied molecular orbital (HOMO) of acetone can primarily be described as lone pair at the oxygen atom with non-bonding character [6]. The molecular geometry is therefore not changed by photoexcitation to Rydberg states or even by photoionization of the HOMO electron [7]. The energies of the ns, np and nd Rydberg series have been accurately determined in synchrotron experiments [8, 9]. These Rydberg states are crossed by valence states, which provide efficient relaxation pathways [7, 10]. Excitation to high-lying Rydberg states shows ultrafast population transfer to lower-lying Rydberg states [11, 12]. After excitation to the energy range of 9.2 eV, corresponding to population of the 5p, 5d, 6s, 6p, 6d, 7s states, IC to the oxygen 3p Rydberg states was observed as one of the relaxation channels [11]. This channel facilitates fragmentation to acetyl ions and methyl radicals, with the fragmentation process happening after the ionizing probe pulse, as was clearly shown [11] by photoelectron–photoion coincidence (PEPICO) detection.

In this work we apply a resonance-enhanced four photon ionization scheme (three-photon excitation and one-photon ionization) at 3.1 eV photon energy with pulse durations in the range of the characteristic time of the IC process. With this scheme we are able to observe the state-specific fragment-to-parent ratios not only of the 3p state as previously [11], but of several lower Rydberg states populated by IC. This allows us to directly determine the activation energy for fragmentation, a quantity of central importance to photofragmentation. Variation of the pulse length in the range of 100–200 fs with positive and negative chirps allows us to investigate and influence the fragmentation behavior. By varying the photon energy we scan the excitation energy across several members of the ns, np and nd Rydberg series and observe the dependence of the fragmentation process on the excitation energy.

PEPICO detection allows us to distinguish different ionization channels and to observe the dynamics and fragmentation behavior of each channel [11]. The PE kinetic energy provides information about the chemical composition and excited state of the molecule at the instant of ionization. It can clearly be distinguished whether fragmentation occurs in the neutral before ionization or in the ion after ionization. Correlation with ion masses for each ionization event allows us to determine the activation energy for fragmentation, thereby also providing insight into the redistribution of vibrational energy.

Experimental

The setup consists of a commercial 800 nm Ti:sapphire laser system (Coherent Vitara oscillator and Legend Elite Duo amplifier) that delivers 25 fs, 4 mJ pulses with 80 nm bandwidth at a 3 kHz repetition rate. Wavelengths in the range of 390–415 nm (3.18–2.99 eV photon energy) with a bandwidth of typically 30 meV (full width at half maximum, fwhm) were generated by frequency doubling in a 500 μm thick BBO crystal. The photon energy was varied by tilting the crystal axis to obtain the desired phase-matching condition. The duration and temporal chirp of the SHG pulses were changed by changing the chirp of the fundamental near-IR pulses with the grating compressor of the chirped-pulse amplification system. The SHG temporal pulse profile was characterized with self-diffraction frequency resolved optical gating [13] and the compressor settings were adjusted in order to obtain the desired SHG pulse parameters. The pulses were focused with a 500 mm lens into the vacuum chamber, which contained acetone (purity: >99.9%) at a partial pressure of typically 4.5 × 10⁻⁶ mbar. The generated ions and electrons were detected in coincidence with a PEPICO spectrometer, which consists of a single 0.5 m time-of-flight tube and a repeller electrode with a pulsed extraction field [14]. For electrons, a magnetic bottle configuration in combination with a small extraction voltage (−3 V) was used to obtain a 4π Sr collection efficiency [15]. The energy resolution for electrons was estimated as ΔE/E = 4% [16], which, in combination with the spectral width of the four-photon transition, gives an expected fwhm of the peaks in the electron spectra of about 150–200 meV. In order to extract the ions, a high voltage pulse (+2 kV) was applied to the repeller electrode about 100 ns after the laser pulse. Under these conditions the ion spectra show a mass resolution of Δm/m < 1%, which is sufficient to clearly identify hydrogen separation from acetone, the smallest possible mass difference in this experiment.

Electrons and ions were detected with a dual stage microchannel plate detector. Signal pulses were decoupled from the anode, digitized by a high-speed digital-to-analog converter card (Gage Cobra, Dynamic Signals LLC), and analyzed by constant threshold discriminator and coincidence algorithms. The intensities of the pulses and the acetone particle density were chosen to obtain an ionization rate of about 0.3 events per laser pulse, resulting in a probability for false coincidences of typically 5% [17]. Since all interpretations are based on spectral signatures that are significantly larger, we accept this true-to-false ratio in favor of reduced data acquisition times.
Results and discussion

Peak assignment

Ionization of acetone molecules with laser pulses of 3.1 eV photon energy (~400 nm wave length) and 100–200 fs pulse duration results almost exclusively in the formation of unfragmented acetone parent ions (C₅H₇O⁺, 58 amu) and acetyl fragment ions (C₂H₃O⁺, 43 amu). Figure 1 shows PE spectra recorded in coincidence with parent ions (red line) and in coincidence with acetyl fragment ions (blue line). Both the parent and fragment PEPICO spectra consist of several peaks, which can be assigned to one-photon ionization from different Rydberg states. These are populated either directly by three-photon excitation from the ground state, or by IC to lower Rydberg states, as indicated in figure 2. IC can proceed directly between Rydberg states that are close in energy [18], or via valence states that cross the Rydberg states and provide efficient relaxation pathways [7, 10] (orange dotted arrow in figure 2). We note that the shape of the spectra cannot be explained with ionization originating from one Rydberg state and leading to vibrational excitations in the ion, because the most dominant vibrational modes activated by photoexcitation are too low in energy (the CCC deformation \( \nu_{19} \) and CO in-plane bending \( \nu_{19} \) with respective excitation energies of only 39 and 51 meV) [8].

Table 1 lists the observed PEPICO peak positions (\( E_{e,kin} \)) together with the level assignments and deviations (\( E_n - E_{n, lit} \)) to line positions obtained from high precision synchrotron experiments [8, 9]. For electron energies up to \( E_{e,kin} = 2.25 \) eV a single Rydberg state can be assigned to each PE peak (with exception of the closely spaced 3p, 3p, 3p, and 3p, 3p states). Above \( E_{e,kin} = 2.35 \) eV, where the energetic distance of states drops below the three-photon bandwidth, we group the \( n_p, n_d, \) and \( (n + 1)s \) states to obtain a Rydberg series, each member of which is assigned to one PE peak. For simplicity, we label these groups \( S_{n1}, S_{n2}, \) and \( S_{n4} \) (table 1). Some states, which are represented as weak shoulder and barely visible in figure 1, can be better identified

| \( E_{e,kin}/eV \) | \( E_n/eV \) | Assignment | \( E_{n, lit}/eV \) | \( E_n - E_{n, lit}/eV \) |
|-----------------|-------------|-----------|-----------------|------------------|
| 2.95            | 9.52        | \( S_{n1} \) (7p, 7d, 8s) | 9.41            | 0.11             |
| 2.70            | 9.27        | \( S_{n3} \) (6p, 6d, 7s) | 9.30            | 0.03             |
| 2.55            | 9.12        | \( S_{n2} \) (5p, 5d, 6s) | 9.10            | 0.02             |
| 2.35            | 8.92        | \( S_{n1} \) (4d, 5s)    | 8.83            | 0.09             |
| 2.25            | 8.78        | 4d\( \nu_{2} \)         | 8.70            | 0.08             |
| 2.05            | 8.62        | 3d\( \nu_{2} \), 4p\( \nu_{2} \) | 8.58           | 0.04             |
| 1.70            | 8.27        | 4 s             | 8.22            | 0.05             |
| 1.60            | 8.17        | 3d\( \nu_{2} \)         | 8.17            | 0.00             |
| 1.35            | 7.92        | 3d\( \nu_{2} \)         | 8.09            | 0.17             |
| 1.15            | 7.72        | 3d\( \nu_{2} \)         | 7.72            | 0.00             |
| 0.90            | 7.47        | 3p\( \nu_{2} \), 3p\( \nu_{2} \) | 7.40           | 0.07             |
| 0.70            | 7.27        | Prob. valence     |                |                  |
| 0.45            | 7.02        | Prob. valence     |                |                  |
| 0.25            | 6.82        | Prob. valence     |                |                  |
| 0.10            | 6.67        | Prob. valence     |                |                  |

Figure 1, shows PE spectra recorded in coincidence with parent ions (red line) and in coincidence with acetyl fragment ions (blue line). Both the parent and fragment PEPICO spectra consist of several peaks, which can be assigned to one-photon ionization from different Rydberg states. These are populated either directly by three-photon excitation from the ground state, or by IC to lower Rydberg states, as indicated in figure 2. IC can proceed directly between Rydberg states that are close in energy [18], or via valence states that cross the Rydberg states and provide efficient relaxation pathways [7, 10] (orange dotted arrow in figure 2). We note that the shape of the spectra cannot be explained with ionization originating from one Rydberg state and leading to vibrational excitations in the ion, because the most dominant vibrational modes activated by photoexcitation are too low in energy (the CCC deformation \( \nu_{19} \) and CO in-plane bending \( \nu_{19} \) with respective excitation energies of only 39 and 51 meV) [8].

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The proposed assignment agrees very well with the line positions documented in literature and the deviation \((E_n - E_{n,\text{lit}})\) of the observed PEPICO peak positions is with one exception less than the experimental resolution of \(\sim 150\text{ meV}\) (spectrometer resolution and laser bandwidth). We note that the \(np_a\) \((n > 3)\), \(nd^2\), \(nd_c\) states are not included in our assignment because no exact state energies are available, as their excitation is symmetry forbidden with single photon excitation from the ground state \([8, 9]\).

Three-photon excitation with 3.14 eV photon energy provides a total excitation energy of 9.42 eV. Considering the 33 meV fwhm spectral bandwidth, the \(S_{n3}\) \((7p, 7d, 8s)\) and \(S_{n3}\) \((6p, 6d, 7s)\) states can be excited (table I, figure 1), which are represented by the parent PEPICO peaks at 2.95 and 2.70 eV, respectively. The parent and fragment PEPICO spectra in figure 1 clearly show PE peaks below 2.70 eV, which we assign to the members of the \(ns\), \(np\) and \(nd\) Rydberg series, as listed in table I. Above 2 eV the PE peaks are detected mainly in coincidence with parent ions, while below 2 eV the fragment PEPICO signal dominates. This important fact provides information about the fragmentation behavior and will be considered below. Beforehand, it is important to discuss the mechanisms leading to population of these lower Rydberg states. Since the HOMO electron has nonbonding character, the molecular symmetry of the ground state is very similar to that of the corresponding Rydberg states, as well as to the symmetry of the lowest ionic state. Therefore, the potential energy surfaces of these states appear to be parallel \([7]\) and vibronic 0–0 transitions are dominant \([18]\), as indicated in figure 2. The laser bandwidth is too narrow to excite 0–0 transitions to Rydberg states below \(S_{n3}\). States below 9.27 eV \((S_{n3})\) are thus populated by electron relaxation through IC \([7, 10, 18]\) (orange arrow in figure 2). Because IC can be a very fast process on sub-10 fs time scales \([3]\), relaxation to and ionization from lower Rydberg states will proceed within the same laser pulse if the pulse duration is on the order of or longer as the IC time constant. IC populates different vibrationally excited lower Rydberg states, each of which is ionized to the corresponding vibrationally excited state of the ionic ground state, because the potential energy surfaces are parallel. This is indicated in figure 2: for example, the photoexcited \(S_{n3}\) states in low vibrational levels are ionized to the same low vibrational levels of the ion, while IC to \(S_{n3}\) results in energy conversion to vibrations and consequently to ionization to vibrationally higher excited ionic states. The energetic distance of the respective Rydberg state to the ionic state, the \(IE\), is obtained from the observed PE kinetic energy. The lower in energy the observed PE peak is, the more energy is deposited in the molecule and converted to vibrations.

Ionization of states above 4p (2.05 eV) leads primarily to unfragmented parent ions, while ionization of states below 4p is dominated by fragmentation. It is important to realize that fragment PEPICO peaks are observed at PE energies that

**Figure 3.** Acetone parent PEPICO (a) and fragment PEPICO (b) spectra obtained with different photon energies, as given in the legend. As in figure 1, ionization is achieved by a resonant \(3 + 1\) photon transition. The pulse length was 150 fs (positive chirp) and the spectral bandwidth varied between 33 and 44 meV. The fragment and parent spectra at each photon energy are normalized to the highest parent signal. For clarity, the fragment spectra (b) are vertically offset by 0.05. Vertical lines indicate the highest-energy IC to Sn3 results in coincidence with parent ions, while below 2 eV the fragment PEPICO signal dominates. This important fact provides information about the fragmentation behavior and will be considered below. Beforehand, it is important to discuss the mechanisms leading to population of these lower Rydberg states. Since the HOMO electron has nonbonding character, the molecular symmetry of the ground state is very similar to that of the corresponding Rydberg states, as well as to the symmetry of the lowest ionic state. Therefore, the potential energy surfaces of these states appear to be parallel \([7]\) and vibronic 0–0 transitions are dominant \([18]\), as indicated in figure 2. The laser bandwidth is too narrow to excite 0–0 transitions to Rydberg states below \(S_{n3}\). States below 9.27 eV \((S_{n3})\) are thus populated by electron relaxation through IC \([7, 10, 18]\) (orange arrow in figure 2). Because IC can be a very fast process on sub-10 fs time scales \([3]\), relaxation to and ionization from lower Rydberg states will proceed within the same laser pulse if the pulse duration is on the order of or longer as the IC time constant. IC populates different vibrationally excited lower Rydberg states, each of which is ionized to the corresponding vibrationally excited state of the ionic ground state, because the potential energy surfaces are parallel. This is indicated in figure 2: for example, the photoexcited \(S_{n3}\) states in low vibrational levels are ionized to the same low vibrational levels of the ion, while IC to \(S_{n3}\) results in energy conversion to vibrations and consequently to ionization to vibrationally higher excited ionic states. The energetic distance of the respective Rydberg state to the ionic state, the \(IE\), is obtained from the observed PE kinetic energy. The lower in energy the observed PE peak is, the more energy is deposited in the molecule and converted to vibrations.

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correspond to ionization from Rydberg states of the unfragmented acetone molecule. In fact, all fragment PEPICO peaks are also recognizable in the parent PEPICO signal. The electron kinetic energy, as observed in the spectrum, is determined by the chemical nature of the molecule at the instant of ionization. Assignment of the acetyl fragment PEPICO peaks to excited states of the unfragmented acetone proves that the fragmentation process has not happened at the moment of ionization, but occurs in the ionic ground state after ionization.

The fragment PEPICO peak at 0.90 eV is assigned to the states 3p\(_x\), 3p\(_y\), 3p\(_z\), which lie within 100 meV. The 3p states have been observed in previous experiments, further supporting our assignment. Because the next lower state to 3p is the 3s state at 6.37 eV, it is too low in energy to be ionized with one photon, the PEPICO peaks below 0.90 eV could be, in part, related to a Norrish Type I dissociation of the neutral molecule with subsequent ionization of the acetyl radical. Alternatively, a relation to valence states is possible: an avoided crossing of the 3\(\pi\) with the valence (\(\pi \rightarrow \pi^*\)) state leads to a double minimum potential, and thus to ionization of the \(\pi \rightarrow \pi^*\) state to the first excited ionic state, which in turn yield a lower electron kinetic energy.

The superior signal-to-noise ratio obtained with the resonance-enhanced four-photon ionization scheme of this work allows us to observe the weaker PE peaks above 3p, which was not possible in previous experiments. In these studies the signal was obscured by a pump-probe correlation signal for time delays below 300 fs. Above this limit the pump-probe signal was weak because the majority of the population has decayed, resulting in a poor signal-to-noise ratio. Here, the spectra obtained with single pulses provide a good contrast for the closely spaced PE peaks between 1 and 2 eV. This enables us to scan the excitation wavelength and observe the shift of the fragment-to-parent crossover, in order to obtain a deeper insight into the fragmentation dynamics and to determine the threshold energy required for fragmentation more precisely.

Wavelength variation

PEPICO detection clearly shows whether ionization from a certain excited state leads to fragmentation or not. For states that are populated by IC the amount of energy that is converted into vibrational energy (\(\Delta E_{vib}\)) can be determined from the photon energy and the electron kinetic energy. In order to determine \(\Delta E_{vib}\) we recorded PEPICO spectra for different photon energies, as shown in figure 3. Most obvious, the parent PEPICO spectrum (figure 3(a)) shows a strong dependence on the photon energy, while the fragment spectrum (figure 3(b)) shows minor but nevertheless very important changes in the range of 1.5–2.5 eV. We first discuss the parent spectra before we determine \(\Delta E_{vib}\) from the fragment spectra.

Table 2. Photon energies and energy considerations for the PEPICO spectra in figure 3. \(h\nu\) … photon energy; \(E_{max}\) … position of the highest-energy IC fragment peak in the PEPICO spectrum (figure 3(b)); \(S_n\) … Rydberg state corresponding to \(E_{max}\). \(\Delta E_{vib} = 4h\nu − (IE + E_{kin})\)… energy deposited in the molecule.

| \(h\nu/eV\) | \(3h\nu/eV\) | \(E_{max}/eV\) | \(S_n\) | \(\Delta E_{vib}/eV\) |
|-----------|-------------|----------------|--------|----------------------|
| 2.99      | 8.97        | 1.35           | 3d\(_{\pi^*}\) | 0.91                |
| 3.02      | 9.06        | 1.60           | 3d\(_{\pi}\)  | 0.78                |
| 3.06      | 9.18        | 1.70           | 4s      | 0.84                |
| 3.10      | 9.30        | 2.05           | 4p      | 0.65                |
| 3.14      | 9.42        | 2.05           | 4p      | 0.81                |
| 3.18      | 9.54        | 2.25           | 4d\(_{\pi}\) | 0.77                |

The stepwise photon energy increase enables the excitation to successively higher Rydberg states. For example, with 8.97 eV excitation energy (photon energy \(h\nu = 2.99\ eV\)) the 4p states at 8.58 eV are excited and appear as dominant peak at 2.05 eV in the parent spectrum (blue line in figure 3(a)). Increasing the excitation energy to 9.30 eV (\(h\nu = 3.10\ eV\), cyan curve in figure 3(a)) results in additional ionization from 4d\(_{\pi^*}/S_{n1}\) and 5s\(_{\pi^*}/S_{n2}\). The highest excitation energy, 9.54 eV (\(h\nu = 3.18\ eV\), yellow curve), facilitates excitation to \(S_{n4}\), with the strongest spectral feature at 2.95 eV. This spectrum additionally has contributions from all lower Rydberg members down to 4s, with decreasing amplitude. Considering the laser bandwidth as above, these states are populated by electronic relaxation (IC) between the \(S_{n}\) states and the Rydberg states below, as will be discussed in more detail below.

The photon energy dependence of the fragment PEPICO spectrum (figure 3(b)) is different from that of the parent. While on the low energy side the positions of all PEPICO peaks remain constant, on the high energy side peaks appear that correspond to increasingly higher states for increasing excitation energies. As clearly seen in figure 1, the fragment PEPICO spectra show relatively large peaks up to a certain energy limit (2 eV) and significantly smaller peaks above. The one of the larger peaks with the highest energy is important for us, as it represents the energy conversion threshold for fragmentation during the IC process. The smaller peaks, in contrast, are caused by a different fragmentation mechanism as we will show by pulse energy dependence measurements below. In figure 3(b), long vertical lines indicate the position of the highest-energy IC fragment peak for different excitation energies, and table 2 lists the corresponding energies \(E_{max}\) and state assignments \(S_n\). The amount of energy \(\Delta E_{vib}\) that is converted into vibrational energy during the IC process can be calculated as difference between the energy of the four photons required for ionization and the IE plus the measured electron kinetic energy: \(\Delta E_{vib} = 4h\nu − (IE + E_{kin})\). The lower limit of \(\Delta E_{vib}\) required for fragmentation is thus obtained from the highest-energy IC fragment peak in the PEPICO spectrum (table 2) and is indicated by the lengths...
of horizontal arrows in figure 3(b). For example, for $\nu = 2.99 \text{ eV}$ (blue curve in figure 3(b)) we identify the highest fragment peak at 1.35 eV, meaning that IC to 3d$^2$-$\pi_1$ yields fragmentation and $\Delta E_{\text{ vib}}$ is determined to be 0.91 eV. The average of $\Delta E_{\text{ vib}}$ over the six measurements with different photon energies is $(0.79 \pm 0.04) \text{ eV}$, which we take as the activation energy for fragmentation.

As a side note, we mention that the highest excitation energy of 9.54 eV ($\nu = 3.18 \text{ eV}$) results in two peaks at very low kinetic energies emerging in both the parent and fragment PEPICO spectra (figure 3). The parent and fragment peaks are of a different origin as becomes clear from the spectra for even higher excitation energies of 9.67 eV (not shown). The parent peak at 0.1 eV is due to direct ionization with three photons, because the energy of three photons including the bandwidth is sufficient to reach the ionization potential of 9.708 eV [8]. Consequently, this peak grows significantly in the 9.67 eV spectrum. The fragment PEPICO signal, in contrast, shows a double peak structure and increases much less at 9.67 eV. We assign this peak to another relaxation-fragmentation channel that involves fragmentation of the neutral acetone molecule to an acetyl and methyl fragment in combination with subsequent ionization of the acetyl [11]. This channel seems to be weakly present for lower excitation energies and increases strongly for higher energies.

**Pulse length variation**

The results up to now have shown that IC leads to a population of states that are energetically below the states in the excitation window. Depopulation of the Rydberg states in this energy range was assigned with a time constant of $(147 \pm 28) \text{ fs}$ [11]. Variation of the pulse duration in the range of 100–200 fs should therefore influence the PEPICO spectra. While the alteration is minor for the parent spectrum (figure 4(a)) and recognizable only for negatively chirped pulses (green and blue trace), it is much stronger for the fragment spectrum (figure 4(b)). All fragment peaks grow significantly in size for longer pulses because more time is available for IC to proceed before ionization, resulting in increased fragmentation. This demonstrates that the Rydberg states up to 4p (2.05 eV peak) are populated by IC within the temporal range of the mentioned time constant. Note that the 4p states (2.05 eV peak) were determined as the highest relaxed states that lead to fragmentation for this photon energy (see figure 3 and table 2).

The increased fragmentation rate for longer pulses is also recognizable in figure 5(a), where the integrated fragment-to-parent ratio is plotted as function of the pulse length of positively (red) and negatively (blue) chirped pulses of 3.14 eV photon energy. It is immediately evident that the relaxation and fragmentation behavior is influenced by the sign of the chirp. Negatively chirped pulses, with the blue end of the spectrum advancing the pulse, lead to more efficient fragmentation than their positively chirped counterparts. For lower photon energies of 2.99 eV, in contrast, the integrated fragmentation ratio is independent of the chirp (not shown). This leads us to the following interpretation: The density of Rydberg states is higher in the energy region accessed with 3.14 eV, as compared to excitation with 2.99 eV (see table 1). With a higher density of states, the advancing blue part of a negatively chirped pulse is able to trigger different and more efficient relaxation pathways compared to the trailing red part. This is not the case if the average distance between states is larger than the spectral width of the pulse. Hence, the chirp dependence is observable with 3.14 eV but not with 2.99 eV photon energy. We also note that different responses to positively and negatively chirped pulses is often a signature for coherent control of molecular processes. However, in this case the chirp dependence is based on pure energy arguments.

The parent PEPICO spectrum in figure 4(a) shows a clear increase of the 0.9 eV peak, corresponding to the 3p states, for the longest, negatively chirped pulses. This is remarkable, because almost 2 eV are converted to vibrational energy at this photon energy and a considerable fraction of the molecules does not undergo fragmentation. This is in accordance with our previous observations, where two-photon excitation (4.61 eV photon energy) and a time-delayed ionization (3.07 eV) lead to the same parent PEPICO peak for the 3p states, with a fragment-to-parent ratio of 2.7 [11]. We find that the height of the 3p parent peak increases by about 400% within the observed pulse length range, while the corresponding fragment peak only doubles. This is clearly expressed by the fragment-to-parent ratio of the 3p peak, as shown in figure 5(b). While the ratio initially increases equally with the pulse length for short pulses, it drops dramatically for longer pulses with negative chirp. In order to separate the influence of photon energies from that of the pulse chirp, we carried out pulse length variations with lower photon energies (2.99 eV), where this effect was not observed: the 3p parent signal is low and does not increase for negatively chirped pulses. These results lead us to the interpretation that a different IC relaxation pathway is accessed by the high photon energies at the beginning of the negatively chirped 3.14 eV pulse. Due to saturation, the high photon energies are able to activate these new pathways more strongly when they come at the beginning of a negatively chirped pulse as compared to a transform limited or positively chirped pulse. These pathways must...
Figure 6. Pulse energy dependence of the parent (red triangles) and fragment (blue circles) PEPICO signals obtained with 3.14 eV photon energy. The signal is integrated over a bin size of 200 meV for each data point. The inset shows the actual energy dependence of parent (triangles) and fragment (circles) signals at the characteristic PE energies of 0.9 and 2.7 eV, in a log–log plot.

Proceed along different relaxation routes with different non-adiabatic couplings. Although the same amount of (or even more) energy is converted to vibrations, the redistribution of vibrational energy from the initially excited normal modes to other modes is different. Apparently, the CC stretch mode that finally leads to the breaking of the CC bond [7] receives less energy in the relaxation paths originating from Rydberg states at about 9.5 eV, as compared to relaxation from slightly lower states. In this context it is important to note that no other fragmentation pathways, such as hydrogen separation from the acetone cation (mass peak at 57 amu), which would release energy, or the appearance of C_2H_2O^- (42 amu), were identified.

Pulse energy dependence

Finally, we determine the pulse energy dependence of the PEPICO fragment and parent peaks.

Fragmentation in the ion can, in addition to energy conversion during IC in the neutral, be caused by absorption of additional photons after the ionization process [2, 20]. These two mechanisms cannot be distinguished in a single PEPICO spectrum. Since fragmentation due to subsequent excitation of the ion requires the absorption of at least one more photon, the two mechanisms show different pulse energy dependencies of the corresponding PEPICO signals. The number of photons involved in the ionization pathway leading to a certain ion can be obtained from the slope of the PEPICO energy dependence in a log–log plot. The inset of figure 6 shows the pulse energy dependence of the fragment and parent PEPICO signals corresponding to the two main structures in the spectrum at 0.9 eV (3p) and at 2.7 eV (S_5^+: 6p, 6d, 7s). Similar slopes were measured for the PEPICO signals over the whole PE energy range and are shown in figure 6.

In the energy region above 0.9 eV, where the PEPICO peaks have been assigned (table 1), slope values between three and four are obtained for both parent and fragment signals. These slopes represent the three-photon excitation and one-photon ionization path (see figure 2), showing that no additional photon absorptions are involved in the process leading to both the parent and fragment ion. Non-integer slope values (figure 6) can be explained by the laser focus intensity distribution in the ionization region in combination with saturation effects.

Above 2.2 eV a significant rise of the process order for the fragment ion is observed. This sudden increase can be compared to the results obtained above: considering the average energy conversion threshold of \( \Delta E_{\text{vib}} = (0.79 \pm 0.04) \text{ eV} \) and the photon energy, fragmentation is expected for PEPICO signals below 2.1 eV \( (E_{\text{e,kin}} = 4h\nu - (IE + \Delta E_{\text{vib}}) \) see table 2); thus, the fragment PEPICO signal above 2.1 eV, in particular the 2.7 eV fragment peak (figure 1), must be related to subsequent excitation of the ion [2, 20], which explains the observed rise of the process order in figure 6. The probability of the subsequent excitation channel is lower compared to the relaxation channel, as shown by the smaller fragment PEPICO signal at 2.7 eV compared to 2.0 eV and below (figure 1).

Summary and conclusions

The fragmentation behavior caused by ultrafast nonadiabatic energy conversion from electronic to nuclear vibrational motion has been investigated in acetone molecules. We apply resonance-enhanced four-photon ionization consisting of a three-photon excitation to high-lying Rydberg states and a one-photon ionization (figure 2). Although only a few states lie within the three-photon excitation bandwidth, the PEPICO spectra show that a multitude of lower Rydberg states is populated. IC from the excited states to lower Rydberg states proceeds so fast that population from the lower states is ionized within the same laser pulse. Energy conversion to vibrational modes during IC in combination with intramolecular vibrational energy redistribution leads to fragmentation of the molecule after the ionization event.

By coincidence detection of the electron kinetic energy and the ion fragment for each ionization event, we were able to fully characterize the fragmentation behavior and its dependence on the photon energy (excited state), pulse duration and chirp, as well as pulse energy.

The activation energy for fragmentation, which we determine as the smallest amount of energy conversion required to facilitate fragmentation, was determined to be \( (0.79 \pm 0.04) \text{ eV} \). Below this threshold the PEPICO spectra are dominated by parent signals and above this threshold fragment signals prevail. As the IC time constant is in the range of the pulse duration [11], the relaxation probability increases with longer pulses, yielding increased fragmentation. Our value for the activation energy agrees very well with results obtained from synchrotron experiments, where vibrationally excited cations are produced by one-photon ionization with photon energies above the \( IE \) [21, 22]. The breakdown curves for acetone ions and acetyl ions show that
an excess energy of 0.79 eV above the IE results in fragmentation of about 90% of the acetone ions [22]. Furthermore, the calculated energy for dissociation of neutral acetone to an acetyl and a methyl radical is 3.61 eV, whereas for dissociation of the ground state acetone ion to an acetyl ion and a neutral methyl radical it is only 0.84 eV [23]. This is in perfect agreement with the experimental dissociation energy we observe and agrees with our interpretation that dissociation occurs after ionization and not ionization after dissociation, which could not be distinguished with less selective methods than PEPICO. Furthermore, the energetic barrier for dissociation in the ionic state, as predicted by simulations [23], indicates that the energy conversion during IC directly leads to fragmentation, without additional processes being active.

Surprisingly, excitation energies of 9.5 eV with negatively chirped pulses lead to suppression of fragmentation despite a significantly higher energy conversion of 2.0 eV, as documented by a significant increase of the parent PEPICO signal associated to the 3p states. This indicates that additional relaxation pathways are available for excitation to increasingly higher Rydberg states, because these interact with higher valence states [6]. The redistribution of vibrational energy along these pathways seems to be different as it transfers less energy to the CC stretch mode, thereby reducing the fragmentation probability.

Finally, we find with pulse energy variations that subsequent excitation of the ion, which also leads to fragmentation by depositing additional energy directly in the ion, plays a minor role. These results demonstrate that in the complex situation of multiple relaxation pathways, the high selectivity of PEPICO detection is a prerequisite to disentangle the pathways and observe their fragmentation behavior. This is the case for applications based on multiphoton excitation.

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