Photophysics of indole upon x-ray absorption

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A photofragmentation study of gas-phase indole (C₉H₇N) upon single-photon ionization at a photon energy of 420 eV is presented. Indole was primarily inner-shell ionized at its nitrogen and carbon 1s orbitals. Electrons and ions were measured in coincidence by means of velocity map imaging. The angular relationship between ionic fragments is discussed along with the possibility to use the angle-resolved coincidence detection to perform experiments on molecules that are strongly oriented in their recoil-frame. The coincident measurement of electrons and ions revealed fragmentation-pathway-dependent electron spectra, linking the structural fragmentation dynamics to different electronic excitations. Evidence for photoelectron-impact self-ionization was observed.

David W. Pratt originally initiated our investigations into the photophysics of indole and this paper is dedicated to him on the occasion of his 80th birthday.

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1 Introduction

Indole, the chromophore of the essential amino acid tryptophan, is an ubiquitous part of peptides and proteins. It is the strongest near ultraviolet (UV) absorber in these biological molecules and, for a detailed understanding of the photostability and radiation damage of these biological samples, it is highly relevant to disentangle indole’s intrinsic photophysics, e.g., its various excitation, relaxation, and fragmentation pathways following electronic excitation. Indole was extensively studied using microwave [20] and optical spectroscopy, [11–13] including vibrationally, [14,15] and rotationally resolved [16,17] electronic spectroscopy, and also using time-resolved ion and photoelectron spectroscopy. [18,19] Here, we extend these studies to the investigation of the photophysics and photofragmentation dynamics of indole following soft x-ray absorption.

Fragmentation studies of isolated gas-phase molecules and clusters allow to extract molecular properties, such as the geometric structure. [13,14] Therefore, they provide a link between the laboratory frame and the molecular frame that allows to investigate wave packet dynamics on complex potential energy surfaces through molecular-frame dependent observables such as, for instance, molecular-frame angle-resolved photoelectron spectroscopy (MF-ARPES). [16,17] Furthermore, fundamental relaxation processes like Auger decay, interatomic (intermolecular) Coulombic decay, [18,19] or electron-transfer mediated decay (ETMD) [20] can be investigated upon x-ray ionization, and can be employed as observables to study molecular dynamics. In order to understand the complete fragmentation and charge rearrangement dynamics of molecules and small compound systems such as clusters, coincidence measurements can be highly advantageous. [21] Various techniques were developed during the last years, [22–25] which include photoion-photoion coincidence (PIPIICO), photoelectron-photoion-photoion coincidence (PEPIPICO), or Auger-electron photoion-photoion coincidence (AEPPIPICO) measurements. [24,25] Such coincidence measurements can, at least for simple molecules, be used to study molecular-frame (MF) properties by reconstructing the molecular orientation from the measured three-dimensional (3D) velocity distributions of all charged fragments, which is the recoil-frame (RF) of the molecule. The connection between the RF and the MF requires unique molecular fragments, e.g., “marker atoms,” and prior knowledge about the directionality of the fragmentation to determine the orientation of the molecule within the RF. Studies in the RF include recoil-frame angle-resolved photoelectron spectra (RF-ARPES), [26,27,28] which allow to image molecular orbitals and their temporal evolution during dissociation, [27] or to extract structure and molecular dynamics information by “diffraction from within” [29] type of experiments. For such experiments, it is highly advantageous to locally ionize the molecule at a specific atom, which can be achieved by inner-shell ionization via extreme ultraviolet radiation, soft x-ray, or x-ray radiation. Localized ionization provides also access to the local electronic structure and excited state dynamics. [30–34] and can be used to break specific bonds. [32]

Here, isolated indole (C₉H₇N) molecules were ionized by a single (soft) x-ray photon with an energy of 420 eV, i.e., ~10 eV above the nitrogen 1s ionization threshold, the N(1s) edge. This gives rise to an enhanced localized ionization at the nitrogen atom in the molecule [20] Photo- and Auger elec-

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tron as well as the ionic fragments of indole were detected in coincidence in a double-sided velocity map imaging (VMI) spectrometer (VMIS). \cite{9} Our work provides the first inner-shell photoionization study of bare gas-phase indole. It also provides the basis for relaxation and fragmentation studies of larger indole-containing molecules, e.g., tryptophan, as well as molecular clusters, such as the investigation of intermolecular interactions in indole–water \cite{10,11} or indole–ammonia. \cite{12} In fact, the experiment described here was set up such that the photofragmentation of indole and indole–water clusters could both be measured. Our findings for the photochemistry of indole–water clusters are beyond the scope of this manuscript and will be presented in an upcoming publication. \cite{13,14}

## 2 Experimental setup

Figure 1 shows the experimental setup, including a species-selecting molecular-beam injector. \cite{15,16} A supersonic expansion of a few mbar of indole seeded in 60 bar of helium was provided by a pulsed Even-Lavie valve. \cite{17} The valve was operated at a repetition rate of 250 Hz and a temperature of 110°C. The deflector was used to spatially separate different species in the expansion, including a separation of indole from the helium seed gas.

The molecular beam apparatus was mounted to the CFEL-ASG Multi-Purpose (CAMP) endstation, \cite{18} which was connected to the Petra III synchrotron's variable polarization beamline P04 \cite{19} (circular polarization > 98%, 5·10^13 photons/s, 480 bunches, 16 ns bunch spacing). The molecular beam was crossed by the 420 eV (λ = 2.95 nm) synchrotron radiation under an angle of 90 degree inside a double-sided VMIS \cite{20} for simultaneous electron and ion detection. Electrons and ions were detected with a hexanode (electrons) and quadanode (ions) delay line detector (HEX80 and DLD80, RoentDek), respectively. For the data presented, however, the hexanode detector had to be operated as a quadanode due to a defect third delay-line layer. The electronic readout was triggered by the detection of an electron and was set to an acquisition time of 6 µs, which was long enough to detect ionic fragments with an atomic mass (m)-to-charge (q) ratio of up to ~220. The pulse duration of the molecular beam in the interaction region was about 60 µs full width at half maximum (FWHM), resulting in a duty cycle of ~1.5%. A logical gate, synchronized to the arrival time of the molecular beam in the interaction zone, was used to record data in a 200 µs time window, reducing the absolute number of background events. The overall event rate was on the order of a few hundred events per second. The inset of Figure 1 shows the reconstructed temporal molecular beam profile plus a constant offset due to background events. The background events were used as a background correction in, e.g., Figure 2. In addition to the reconstructed molecular beam profile vertical black lines are shown, indicating the pulse structure of the synchrotron.

## 3 Coincidence spectra

The photofragmentation of indole upon single-photon inner-shell ionization from the nitrogen and carbon 1s orbitals was investigated via a coincidence measurement between the emitted electrons and the corresponding ionic fragments. A background subtracted PEPICO spectrum \cite{21,22} of indole is shown in Figure 2 as a function of the atomic mass-to-charge m/q ratio of the first and second detected ion, m_1/q_1 and m_2/q_2, respectively. The molecular structure of indole is shown in the inset of Figure 2. The PEPICO map allows to disentangle different fragmentation channels of indole in the case of at least two detected ionic fragments. Nine principal coincidence regions are observed, which are labeled 1–6, 1∗, 3∗, and 4∗. A detailed list of the identified fragmentation channels is given in Table 1.
Both regions have the same ‘heavy’ second detected ion, i.e.,
are due to fragmentation into three or more fragments, i.e.,
will not be considered, and are not included in the labeling
The missing fragments can be neutral or ionic and the corre-

Table 1 Overview of the identified ion-fragmentation channels extracted from the ion coincidence spectrum shown in Figure 2. The indices i and j in the formulas show the number of hydrogen-atom or proton losses that resulted in separate lines with a spacing of m/q = 1 u/e within a given island. Regions 4–6, and 4* consist of three heavy neutral/ionic fragments, with numerous different possibilities for hydrogen-atom or proton losses, which are thus not listed explicitly.

| Region | Fragmentation type | Fragmentation channel | mass sum (u) | i  | j  |
|-------|-------------------|-----------------------|-------------|----|----|
| 1     | 2h2f              | C_2H_4^+ + C_4NH_2^-   | 112–117     | 0–1| 0–3|
| 1*    | 3h2f              | C_2H_4^+ + C_4N^-     | 114         | 0  | 0  |
| 2     | 2h2f              | C_2NH_2^- + C_4H_2^-  | 112–117     | 0–3| 0–2|
| 3     | 2h2f              | CNH_2^- + C_4H_3^-    | 113–117     | 0–4| 0  |
| 3*    | 3h2b              | CNH_2^- + C_4H_2^-    | 114         | 0  | 0  |
| 4     | 2h3f / 3h3f      | C_2H_3^- + (C_3NH^- or C_2H_4^-) | 86–91     |    |    |
| 4*    | 2h3f / 3h3f      | C_2H_3^- + (C_3NH^- or C_2H_4^-) | 75–79     |    |    |
| 5     | 2h3f / 3h3f      | (C_2H_3^- or C_4NH_2^-) + C_3H_3^+ | 87–91     |    |    |
| 6     | 2h3f / 3h3f / ... | (C_2H_3^- or C_4NH_2^-) + C_3H_3^+ | 61–67     |    |    |

The sum of the masses of the fragments in regions 1–3 is equal to the mass of indole, neglecting the loss of hydrogen/protons. Therefore, these fragmentation channels correspond to the generation of two heavy ionic fragments, which are called in the following a two-hole two-fragment (2h2f) fragmentation channel. They are visually separated from the other channels in Figure 2 by the solid black line. Coincidence regions 4–6, and 4* are due to fragmentation into three or more fragments, i.e., the total masses of the first two detected ions corresponding to a single event do not add up to the mass of the indole monomer. The missing fragments can be neutral or ionic and the corresponding channels are labeled two-hole three-fragment (2h3f) and three-hole three-fragment (3h3f), respectively. Due to a limited detection efficiency, the 3h3f fragments can split into different coincidence regions as, for example, the regions 4 and 4*. Both regions have the same ‘heavy’ second detected ion, i.e., C_1N_2^- or C_2H_5^-, but alternating ‘lighter’ fragments for the first detected ion. If only the ‘lighter’ fragments are detected, or if all ions are detected, this fragmentation channel is, in the used representation, part of region 6. Regions 1*, and 3* have molecular fragments with the same masses as regions 1, and 3, but with different charge distribution, i.e., they contain both, singly and doubly charged ionic fragments and are labeled therefore as three-hole two-fragment (3h2f) channels.

If not stated otherwise, the losses of hydrogens or protons will not be considered, and are not included in the labeling of the different fragmentation channels. Further, 2h2f and 2h3f fragmentation channels are quantified such that they show strong axial recoil, as described in section 4. In contrast, the majority of ions detected in 3h3f fragmentation channels do not show a strong axial recoil. Therefore, if not all ions are detected in a 3h3f fragmentation channel, these channels are distinguished from 2h2f or 2h3f by their axial recoil. Furthermore, due to the stronger Coulomb repulsion between three ionic fragments, the kinetic energy of the 3h3f fragments gives a hint toward these fragmentation channels.

Taking this assumptions into account and assuming an ion detection efficiency ~40 %, the branching ratios between the main regions of the PEPIC/CO spectrum can be estimated to 27 %, 51 %, and 22 % for 2h2f, 2h3f and 3h2f/3h3f, respectively. The detection efficiency of the electrons is neglected, leading to an overestimation of the contribution of 3h2f and 3h3f fragmentation channels. Independent of the electron detection efficiency, the majority of indole molecules is thus fragmenting into three heavy fragments.

If proton and hydrogen transfer processes are neglected, PEPIC/CO region 3 and 3* are the only PEPIC/CO regions for which the ionic fragments can be uniquely assigned, i.e., CNH_2^- + C_2H_5^- corresponding to the (1, 2) and (3, 3a, 4, 5, 6, 7, 7a); see the notation in the inset of Figure 2. In contrast, PEPIC/CO region 1 and 2 consist of a superposition of two fragmentation channels, which can additionally consist of non-unique fragmentation combinations of the indole molecule. Consider, for example, the fragmentation C_1N_2^- + C_4H_2^- + C_2H_4^- + C_2H_4^- of PEPIC/CO region 1. The possible atomic combinations for C_1N_2^- + C_4H_2^- + C_2H_4^- are (1,2,3,3a), (1,2,3,7a), (1,2,7,7a), or (1,2,7,7a). In the case of 2h3f and 3h3f fragmentation channels (regions 4–6) the possible combination of ionic fragments is further increased, resulting in an even lower probability to uniquely assigning the fragments. Exceptions are some single coincidence lines within a coincidence region, such as C_2H_4^- + C_1N_2^- (PEPIC/CO region 1) whose mass sum is equivalent to the mass of the indole molecule, i.e., including the mass of all hydrogens.
4 Fragmentation dynamics

The VMIS is used to measure the projected velocity vectors of the ionic fragments. Figure 3a and b show the VMI images for the first and second detected ion in the coincidence region 4. The corresponding fragments are C\_3H\_3\^+ and (C\_3NH\_2\^+ or C\_2H\_4\^+) or C\_2NH\^+ and C\_3H\_3\^+; the color scale is the same as Figure 2. The velocity of the VMI was calibrated by the helium–photoelectron recoil for different photon energies ranging from 310 to 420 eV. The first detected ions show a slightly higher velocity compared to the second detected ions, which is explained by their smaller mass and the momentum conservation of the fragmenting particles. The increased number of counts visible in the VMI images at v\_x = 0 and v\_z ≈ -2 \cdot 10^2 m/s is due to background from the carrier gas, which is falsely detected at that corresponding TOF window and does not obey momentum conservation. A histogram of the angular relationship between the first and second detected ions is shown in Figure 3c. The angular variations σ\_0₁₂ between the 2D velocity vector of the first detected ion. The blue line shows a Gaussian fit centered at 180° with a standard deviation (SD) of 4.5° for the recoil angle of σ\_0₁₂ = 18.4°. This strong axial recoil between ions in this channel is only observed for a 2h3f fragmentation process (vide infra). This is in agreement with the expected fast fragmentation of the molecule due to Coulomb explosion subsequent to inner-shell ionization, and the momentum conservation between the ionic fragments. σ\_0₁₂ depends on the fragmentation channel, and is σ\_0₁₂ = 12.7° for the 2h2f fragmentation channels, and σ\_0₁₂ = 9.8° and σ\_0₁₂ = 9.5° for the 1° and 3° fragmentation channel, which were assigned to a 2h2f fragmentation channels. These channels show a stronger confinement in the recoil-frame (RF) because they experience a strong Coulomb repulsion, which leads to an RF that is more dominated by Coulomb repulsion. In contrast, a 2h3f fragmentation channel the momentum of the Coulomb repulsion is more in competition with the momentum taken up by the heavy neutral fragment, resulting in a less-confined axial recoil.

The angular variations σ\_0₁₂ in the recoil-frame can be expressed as a degree of (post-)orientation or alignment in the RF, which is \langle \cos^2 \alpha_{2,2D} \rangle \approx 0.98, 0.99, and 0.95, or \langle \cos \alpha_{0,2,2D} \rangle = 0.95, 0.97, and 0.91, for the 2h2f, 3h2f, and 2h3f fragmentation channels, respectively. The angular confinement, i.e., the alignment, is comparable to the best laser alignment experiments \[57\] whereas the directionality, i.e., the orientation, is significantly better. \[57,58\] Thus, in the case of the planar indole molecule, these RF determinations allow for RF-ARPES of the individual ion fragmentation channels, albeit that the actual angular-resolution quality of the ARPES depend on the specific fragmentation channel.

The deviation in σ\_0₁₂ between the 2h2f and 2h3f can be used to estimate the velocity of the neutral fragment. An explicit assignment of the neutral fragments of PEPPIPICO region 4 and 5 is not possible since the neutral fragments cannot be detected. From the tight momentum conservation we infer, however, that the bonds between the neutral and the ionic fragments are broken instantaneously on the timescale of the fragmentation process. In addition, we assume that the missing masses are intact fragments due to the following reasons: First, the ionic fragment dominantly stay intact in the case of a 3h3f fragmentation. Second, there is no dominant PEPPIPICO region where only a single carbon is missing. Then, in the case of coincidence region 4 a mean velocity of 500 m/s can be assigned to a neutral fragment with a mean mass of 27 u.

Figure 4a shows the angular correlation between the ions of a 3h3f fragmentation channel; the second and third detected ions have the same masses as the ions shown in Figure 3, i.e., they correspond to the fragments C\_3H\_3\^+ and (C\_3NH\_2\^+ or C\_2H\_4\^+) or C\_2NH\^+ and C\_3H\_3\^+. The first detected ions were previously neutral and are assigned to the ionic fragments C\_3H\_2\^+ or CNH\^+. The two-dimensional histogram shows the angles α\_0₂ and α\_0₂ between the 2D velocity vector of the second and second-first ion pairs. The definition of the angles with respect to the fragments is visualized by the inset in the top right corner of Figure 4b.

The angular relationship between these pairs of fragments shows an hourglass-like structure, rotated by approximately 45°. Coincidences outside that structure are due to ions, which do not fulfill momentum conservation. This is illustrated by right part of the same histogram, where only ion combinations are shown that do fulfill momentum conservation to a high degree (< 60 u·117 km/s). Figure 4b shows the histogram of the angles α\_0₂ and α\_0₂ for ion pairs that obey momentum conservation, and allows therefore for a better comparison of the recoil angle between the 2h3f and 3h3f. These channels have

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Footnotes:

\[1\] These might be due to a subsequent pulse of the synchrotron radiation ionizing a second particle in the molecular beam within the 6 µs acquisition time window of Figure 1, which has a small but finite probability. Helium contributes strongest to the signal from the molecular beam and is, therefore, the main background signal.
were detected in coincidence with PEPIPICO regions 1–5, 1*, and 2h3f fragmentation channel, and allows therefore to discriminate between both fragmentation channels. This fixed angular relationship between three heavy ionic fragments demonstrates the possibility to reconstruct the three dimensional orientation of the molecule in the laboratory frame provided that the directionality of the moving fragments in the molecular frame are known. Due to the strict planarity of the indole molecule and the immediate Coulomb explosion, the plane of the molecule can be assigned to the recoil plane defined by the three ionic fragments. However, the orientation within the symmetry plane is practically undefined.

5 Angle-resolved photoelectron spectra

Figure 5 a and b show the electron velocity map in a cartesian and a polar coordinate system, respectively. The photoelectron VMI has been calibrated by photoelectrons originating from single-photon ionization of atomic helium and neon, at photon energies between 310 and 980 eV. The labels Q1–Q4 correspond to the four different quadrants of the VMI image; \( v_X \) and \( v_Z \) correspond to the electrons velocity component in the laboratory frame, and \( v_\theta \) and \( \theta \) are the radial and angular coordinate in the polar coordinate system. The electrons were detected in coincidence with PEPIPICO regions 1–5, 1*, and 3h, with a background correction applied by accepting only events within 2\( \sigma \) of the recoil angle of the ions (Figure 3). The 3h3f fragmentation channels of indole have been considered if three ions were detected, if the second and third detected ion were falling into the coincidence regions 4, and 5, and if the ions fulfilled momentum conservation (Figure 4b). Region 6 was not used due to a high number of background ions detected in this coincidence region. The electron VMI images of indole show four distinct electron velocities at 2.4, 7.1, 9.5, and 11.2 \( \times 10^6 \) m/s, which correspond to electron energies of 16, 143, 258, and 358 eV. The additional slow electrons visible in the center of the VMI image are assigned to background and shake-off electrons from the molecule. The electron energy spectrum, shown in the bottom graph of Figure 5, was obtained by an inverse Abel transformation based on the BASEX algorithm of the second and third quadrant of the electron-VMI image. Quadrants one and four were not used, to avoid the influence of the VMI distortions in these quadrants, which are visible for velocities greater than \( \sim 8 \times 10^6 \) m/s, and attributed partially to the non-working layer of the hexanode DLD, possible influence of an magnetic field, or a non well-centered interaction region in the VMI. Considering atomic electron binding energies, the nitrogen and carbon 1s photoelectron energies would be expected at 10.1 and 26.8 eV, respectively. In pyrrole (\( \text{C}_4\text{H}_3\text{N} \)), which corresponds to the five-membered-ring part of indole, the binding energies are chemically shifted and would correspond to photoelectron energies of 14 and 130 eV for nitrogen and carbon 1s, respectively. This is a deviation of less than 5 % between the 1s binding energies in pyrrole and indole, which is within the systematic error of our measurement. The observed C KVV-Auger-electron energies agree with the experimentally observed lines in benzene at 243–267 eV. The N KVV-Auger-electron energies agree with calculated energies of 356–377 eV. Fitted Gaussians, shown by the red line in Figure 5, allow to extract relative intensities of the specific peaks and, thus, ratios of the electron channels. By comparing inner-shell ionization events, the N(1s) and C(1s) Gaussian fits show a 26.1 % probability for localized ionization at the nitrogen atom. A similar probability of 24.8 % is obtained by comparing the Auger electron ratio. Both numbers are slightly higher than the expected probability of 16 % by considering the atomic cross sections of C and N. We attribute this difference to the specific properties of the selected Coulomb explosion channels. The SD of the N(1s) and C(1s) photoelectrons are \( \sigma = 4 \) and \( \sigma = 9 \) eV, respectively, which is attributed to the distortions of the VMIS and the low number of electrons of the VMI image. The chemical-shift variations of the different carbon atoms (~2 eV) and the bandwidth of the synchrotron radiation (0.4 eV) are negligible. The anisotropy parameters for the photo- as well as Auger electrons, obtained from the inverse Abel transformation averaged over the FWHM of the photoelectron line, are \( \beta_{\text{N(1s)}} = 1.1 \) (0.1), \( \beta_{\text{C(1s)}} = 1.7 \) (0.1), \( \beta_{\text{C(Auger)}} = 0.2 \) (0.1), and \( \beta_{\text{N(Auger)}} = 0.2 \) (0.1). The anisotropy parameter of the Auger electrons is consistent with the expected isotropic distribution of electrons in the laboratory frame. The anisotropy parameter for C(1s) photoelectrons is slightly lower and the anisotropy parameter for N(1s) photoelectrons is significantly lower than the one, \( \beta = 2.0 \), expected for ionization out of an s-orbital by circularly polarized radiation. We attribute this lowered asymmetry parameters to the interaction of photoelectrons with the potential of the molecule, but also partly to the non-perfect reconstruction.

6 Electron-ion fragmentation correlation

The measured coincidences between electrons and ions allow to extract the individual 2D electron VMI spectra of the various ionic fragmentation channels. The 2h2f and 2h3f ion fragmentation channels show a spectrum similar to the one shown in Figure 5. The energy spectrum of the 2h2f and 3h3f fragmentation channels yielded no clear results due to low statistics. Therefore, for the 2h2f, 2h3f, 3h2f and 3h3f channels, radial velocities of the electrons 2D VMI images, i. e., projected electron velocity distributions (EVD), for the different ionic channels are...
compared in the following. This time all quadrants of the electron VMI are taken into account. The distortions of the VMI (Figure 5) in quadrant one and four mainly influenced the determined energy for the Auger electrons, which do not have a significant influence on the following discussion. Figure 5a shows histograms of the EVD sorted into the contributions of the ion-fragmentation channels 2h2f (black), 2h3f (red), 3h2f (blue), and 3h3f (green). The histograms are normalized to the total number of counts; the multiplication factors are given by the inset, which shows the VMI image for electrons detected in coincidence with 3h2f and 3h3f fragmentation channels.

The radial EVD for the three-hole fragmentation channels 3h2f and 3h3f, the blue and green lines in Figure 6a, are also similar. In contrast to the 2h2f and 2h3f radial EVD, the strongest peak of the spectrum is at electron velocities close to the N(1s) photoline, and drops-off continuously toward higher electron velocities, with edges at electron velocities corresponding to the carbon 1s photo- and Auger electrons. This overall shift in the electron spectrum toward lower photoelectron energies is attributed partially to a tertiary ionization of indole via electron-impact ionization, and also due to satellite peaks of the photo- and Auger electrons. This is discussed in the second half of the following paragraph based on the angular anisotropy of the electrons.

To extract an angular anisotropy of the electrons radial distribution, the electron VMI is divided into the four quadrants Q1*-Q4* as shown in the inset of Figure 6b; the coordinate system is the same as shown in Figure 5a, but Q1*-Q4* are rotated by 45° with respect to Q1–Q4. With β-parameters of 1.1 and 1.7 for the nitrogen and carbon 1s photoelectrons a larger signal is observed in Q2* and Q4* than in Q1* and Q3*. For Auger electrons, which typically show no anisotropy, the same averaged number of counts is expected for all quadrants. The histograms in Figure 6b show the radial EVD of the anisotropy (Q2* + Q4*) – (Q1* + Q3*) for electrons detected with two and three ionic fragments in coincidence, i.e., the fragmentation channels 2h2f and 2h3f are jointly labeled 2h (black), and the fragmentation channels 3h2f and 3h3f are jointly labeled 3h (blue). The error bars depict the statistical error, the connecting lines serve to guide the eye, and the histograms are normalized to the number of counts. For the 2h fragmentation channels two distinct maxima are visible at electron velocities corresponding to the nitrogen and carbon photoelectrons. The anisotropies of the Auger electrons at vₑ ≥ 7·10⁶ m/s are effectively averaged to zero. The negative values at radial velocities smaller than 1·10⁶ m/s are attributed to non isotropic noise close to the center of the electron VMI. Comparing the number of electrons assigned to the ionization from nitrogen/carbon shows a probability of approximately 20 % for a localized ionization at the nitrogen atom if the negative values are neglected. This is comparable to the ratio determined from the overall photoelectron intensities in section 5 and, again, slightly higher than expected from the atomic cross sections. The blue histogram, on the other hand, shows electrons in coincidence with the 3h fragmentation channels. Here, no clear carbon 1s photoelectron line is visible. Instead, an increased number of electrons is detected at velocities in-between the carbon and nitrogen 1s photoelectron energies. Those electron energies can not be attributed to the earlier determined photo- or Auger electron energy.

§ This energy is determined as the difference between the mean photon energy and the mean summed electron energies, i.e., the sum of photo- and Auger electron energy.
energies. N(1s) photoelectrons do not have enough energy to tertiary ionize indole by electron impact ionization. Also, the contribution from Auger electrons to triply ionize indole can be excluded in this analysis since they do not show an anisotropy in the laboratory frame. Therefore, we attribute those electrons to either inelastically scattered C(1s) photoelectrons and electrons generated by this inelastic scattering through electron impact ionization, or to satellite peaks from the C(1s) photoelectrons. A closer insight is given by the red line in Figure 6h, which shows a scaled difference between the blue and black spectrum. The scaling was done by a normalization of the number of electrons at \( v_r = 6.8 \times 10^6 \) m/s to subtract the highest possible contribution from direct photoelectrons. This difference spectrum shows three main areas: the contribution of the nitrogen 1s photoelectrons and two highlighted red areas, which are assigned to those inelastically scattered carbon 1s photoelectrons, electrons emitted upon impact ionization, and satellite peaks from the carbon 1s photoline. These electrons in the red areas have a velocity of \( v_r = 2.9 - 4.5 \times 10^6 \) m/s (24-58 eV) and \( v_r = 4.7 - 5.7 \times 10^6 \) m/s (63-92 eV). The number of electrons that correspond to these two areas is about the same, and the sum of the mean electron energy of both peaks is 104 eV.

In Figure 6a, the C(1s) Auger- and photoelectrons show a similar behavior, i.e., the 2h fragmentation channels show a prominent peak, which is absent in the 3h fragmentation channels. Therefore, we attribute this change in the radial EVD of Auger electrons also to electron impact ionization or satellite peaks accompanying the Auger electrons.

A quantitative statement about the contribution of the inelastically scattered electrons, electrons from impact ionization, and satellite electrons to the 2h2f and 2h3f fragmentation channels could, in principle, be extracted from their anisotropy parameter. This was not possible due to the low number of detected electrons. Only for C(1s) photoelectrons a lower limit of 43 % can be estimated from Figure 6b by counting the number of inelastically scattered/satellite electrons (red), which are part of the 2h2f and 3h3f channels (blue).

At the given C(1s) photoelectron energy, the atomic cross section for carbon for electron impact ionization and elastic scattering of electrons are both in the order of 200 \( \times \) 10\(^{-22}\) m\(^2\). This implies that elastically-scattered electrons can be detected at comparable signal strengths, e.g., in photoelectron holography experiments. The inelastically-scattered electrons detected here could be separated by an energy-resolving detection scheme, as demonstrated here.

### 7 Conclusion

We have performed a detailed photoionization and photofragmentation study of indole upon single-photon inner-shell ionization at a photon energy of 420 eV. This photon energy was chosen such that indole could be locally ionized at its nitrogen atom. Ionization from C(1s) was also possible and is the dominant ionization process due to the larger number of carbon atoms present in the molecule. Electrons and ions have been measured in coincidence in a velocity-map-imaging mode to extract 2D and 3D velocity vectors of the charged particles.

In the ion-coincidence spectrum of indole, i.e., for the events with more than one ionic fragment observed, indole is fragmenting into two heavy ions and one neutral fragment in 51 % of the cases. These “heavy” fragments contain, almost exclusively, two or more heavier atoms; the loss of hydrogen atoms and protons was also observed, but they were not considered as specific fragments. Fragmentation channels with only two fragments or with three heavy ionic fragments have also been observed and showed contributions of 27 % and 22 %, respectively. The PEPICO spectrum revealed that the unique assignment of a coincidence region to a carbon atom from a specific position in the molecule is rather the exception than the rule.

The ion-VMI images could be used to reconstruct the recoil-frame of the molecules. The fragmentation process was dominated by the Coulomb repulsion of the generated charges. Influence of chemical effects, e.g., the specific potential-energy surfaces, was observed in the recoil frame of the ions for the case of a coexisting heavy neutral fragment. Ion-VMI images of this selected 2h3f fragmentation channel were discussed regarding the velocity of the dissociating neutral fragment, showing that the bonds between the neutral and ionic fragments must be broken instantaneously on the timescale of the fragmentation process, i.e., no meta-stable ionic fragments were observed. Fragmentation channels with three ionic fragments also showed a fixed angular relationship. This allowed us, for these channels, to directly determine the alignment of the molecular plane in the laboratory frame. Therefore, the recoil-frame and thus, due to the symmetry plane of the molecule, the molecular-frame alignment of the molecular plane in the laboratory frame is uniquely recovered. However, in order to fully reconstruct the three-dimensional alignment and orientation of the indole molecule, i.e., also the orientation inside the molecular plane, the direction of the fragments in this plane would have to be known. This would require elaborate theoretical analysis and is beyond the scope of this paper.

The electron-energy spectrum showed four peaks, which were assigned to photo- and Auger electrons resulting from element-specific ionization at indole’s nitrogen as well as carbon atoms. The corresponding asymmetry parameters of these peaks were extracted from an inverse Abel transformation. For the Auger electrons they were isotropic in the laboratory frame, as expected. For the photoelectrons, deviation from the expected asymmetry parameter for photoelectrons from the carbon and nitrogen 1s orbitals have been observed; where “expected” refers to the asymmetry parameter for a single-photon 1s ionization with circularly polarized light. The observed deviation is partly attributed to the interaction of the photoelectrons with the molecular potential, partly due to a non-perfect reconstruction of the asymmetry parameters, as well as deviations due to background signal from slow background and shake-off electrons.

The correlation between ions and electrons showed that different ion fragmentation channels have different electron spectra, i.e., a relationship between the ionization/excitation process, the corresponding electronic states, and the fragmentation process, reflecting the specific potential energy surface. This was shown, for instance, by a comparison of the projected electron energy spectra for the 2h2f and 2h3f fragmentation channels. In this case it was concluded that inner-shell ionization at the nitrogen edge leads to a higher probability for indole to break up into three heavy fragments.

Evidence for secondary electron-impact ionization as well as satellite photoelectrons was observed in the fragmentation channels where three ionic fragments have been measured.
Those channels showed less pronounced photolines, primarily observed for the C(1s) photoelectrons, as well as signals at electron energies where no photoline is expected. In addition, evidence for satellite peaks of the Auger electrons and inelastically scattered Auger electrons was presented.

Since the cross sections for the observed inelastic scattering and elastic scattering are comparable under the experimental conditions, the possibility of photoelectron-holography experiments is confirmed.

The presented data allowed to record RF-ARPES images of strongly post-oriented indole, albeit that the relation of RF and MF is unknown beyond the common symmetry plane. Due to the low number of events per unique fragmentation channels, i.e., fragmentation channels where specific carbon atoms could be assigned uniquely to the ionic fragment, no statistically significant asymmetries of the electron distribution in the recoil frame were observed.

Overall, our results show that the fragmentation channels depend on the different electronic states, i.e., the chemical potential energy surface, whereas the observed velocities of the fragments are not strongly dependent of these chemical details.

Our work provides the basis for fragmentation studies of larger molecules as well as molecular clusters, such as the indole-derivative tryptophan or indole-water clusters. Comparison of the fragmentation channels and dissociation energies will allow to study the role of solvents on the photophysics of indole upon site specific x-ray ionization. Furthermore, the processes observed here provide information on the indole-chromophore-related radiation damage occurring in coherent diffractive imaging of proteins.

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