High-resolution electron - momentum resolved ion coincidence spectroscopy

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Abstract. When molecules are irradiated by x-rays complicated breakup reactions are initiated: inner shell excitation or ionization leads to a cascade of Auger decays resulting in multiple ionization and multiple bond breaks. During the last years high resolution electron - ion coincidence spectroscopy has developed into a standard tool to analyse molecular break-up reaction pathways. If ion pairs or the momenta of the fragment ions are also recorded, a very detailed analysis of the break-up reaction becomes possible. A manifold of interesting processes can be studied. Here we will discuss site specific fragmentation of CH₃F, F₃Si-CH₂-Si(CH₃)₃, F₃Si-CH₂-CH₂-Si(CH₃)₃, and Cl₃Si-Si(CH₃)₃, and electron transfer during the break up of CH₃F.

1 Outline

Highly monochromatic soft x-rays are frequently used to trigger break-up and rearrangement reactions of molecules in the gas phase. In order to understand - or even control - these reactions one needs to monitor the reaction products i. e. the electrons and molecular fragments in detail. Here we discuss the results based on combining a momentum resolving mass spectrometer with a high resolution electron spectrometer in coincidence experiments. The experiments deal with the break up of four different F and Cl containing molecules F₃Si-CH₂-CH₂-Si(CH₃)₃, F₃Si-CH₂-Si(CH₃)₃, Cl₃Si-Si(CH₃)₃, and CH₃F after the absorption of a single soft x-rays photon leading to inner shell ionization. Many different fragmentation pathways compete and an electron-ion or electron-ion-ion coincidence experiment is necessary to (partially) disentangle the processes.

2 Experimental technique

In the electron energy spectra chemical shifts, Auger lines and Doppler shifts due to ultrafast fragmentation were resolved using a commercial dispersive spectrometer SES2002. Under typical
operating conditions in a coincidence experiment  a resolution of up to 500 meV at 600 eV kinetic energy is feasible. The electrons come from a field free source region as no extraction filed is used for the electrons. In order to resolve all different masses of the ionic fragments from a molecule of medium size a mass range up to 200 amu and a resolution of 1/200 is necessary. Therefore an electric extraction field of about 100 V/cm is applied and the masses are resolved but their different Times Of Flight (TOF) after passing a 650 mm long drift tube. The use of a reflectron configuration ion TOF spectrometer is not possible, as it would remove all momentum information from the TOF of the ions. In order to combine the mass spectrometer with the high resolution electron spectrometer, one needs to use pulsed extraction fields [1-5] that are applied after the electron is detected by a fast position resolving delay line detector (DLD).

Figure 1. Cross section through the experimental setup.

Energetic ionic fragments may hit the ion detector far off axis, so a large position resolving delay line detector (DLD) with 80 mm active diameter is used for the ion detection. In order to further increase the kinetic energy range of the ions with 4π collection efficiency and to demagnify the image of the source region on the detector, ring shaped lenses were put into the drift tube of the ion TOF spectrometer. So e.g. N ions with a kinetic energy up to of 7 eV can be detected with 4π collection efficiency. Making use of the multi-hit capability of the ion detector we recorded electron-ion-ion (e-I-I) coincidences. In medium size molecules like F3Si-CH2-CH2-Si(CH3)3 [6] several hundred different ion pairs can occur and the contribution of random coincidences to the e-I-I coincidence signal can be significant and non-trivial in nature. Therefore an automatic reference measurement and subtraction procedure for the contributions of the random coincidences was developed [7].

3 Site specific fragmentation

The original idea of site specific fragmentation is that the creation of a localized core hole at a specific atomic site inside a molecule will weaken the local bonds because the Auger decay potentially removes two electrons from a bond next to the atom with the core vacancy. It turns out that this idea needs substantial modification for the following reasons: first, the valence orbitals taking part in the Auger decay can be delocalized and therefore have not only significant overlap with many different core orbitals but can also contribute to more than one bond in the molecule. Second, the creation of the core hole can lead to substantial nuclear motion before the Auger decay and therefore the corresponding Auger decay branching ratios to the different electronic final states can happen outside of the Franck-Condon region. As the nuclear motion depends on the core hole site, it can lead to additional site specificity in the partial ion yield. Third, the core ionization and Auger decay can lead to a redistribution of the electrons including charge transfer from one fragment to
another. Such a process involves transitions from one electronic state to another after the Auger decay, therefore the ion yield cannot be understood using wave packets that travel on the potential surfaces of the individual Auger final states.

Figure 2. Mass spectra of fragment ions from F₃Si-CH₂-CH₂-Si(CH₃)₃ after irradiation with 400 eV soft x-rays. The ions that were detected in coincidence with F-side Si 2p photoelectrons, are drawn in the positive direction. Those detected in coincidence with CH₃-side Si 2p photoelectrons are drawn in the negative direction. The inset shows a spectrum of Si 2p electron counts vs binding energy.

For the creation of localized core holes two different experimental methods can be used: one can choose a photon energy for resonant core excitation and therefore preferentially select one core hole site inside the molecule, or alternatively one can use non-resonant photoionization combined with electron spectroscopy to find out which site was ionized in each individual molecule. Inner shell ionization leads to doubly charged Auger final states, therefore the coincident detection of an electron and an ion pair is desirable. Using core ionization one can choose between detecting the photoelectron or an Auger electron. The measurement of the photoelectron energy allows to determine the site of the core ionization, while the measurement of the Auger electron energy determines the Auger final state. The coincident e-I-I measurements are called PEPICICO and AEPICICO, respectively. The ultimate experiment that detects the photo electron, the Auger electron and the ion pair in coincidence (PEAEPIICO) is not feasible with the experimental technique presented. In order to measure the effects due to the localization or delocalization of the valence orbitals on site specific fragmentation, the experiments were performed for three different molecules: F₃Si-CH₂-CH₂-Si(CH₃)₃, F₃Si-CH₂-Si(CH₃)₃, and Cl₃Si-Si(CH₃)₃. The more straightforward choice for the third molecule would have been F₃Si-Si(CH₃)₃. However this molecule is chemically unstable. Details of the AEPICICO results for F₃Si-CH₂-CH₂-Si(CH₃)₃ are presented in reference [6]. Here we will concentrate on the PEPICICO results for all three different molecules. The analysis of the obtained data starts with the photoelectron spectra. The energy needed to remove a Si 2p electron from F₃Si-CH₂-CH₂-Si(CH₃)₃ is 110 eV or 106 eV, depending, if the core ionized Si atom is bound to 3 F atoms or 3 CH₃ groups. This chemical shift is detectable as a difference of 4 eV in the kinetic energy of the photoelectrons. Therefore two distinct peaks for the F-site ionization and the CH₃-site ionization appear in the electron energy spectrum, shown as a small inlet in figure 2. This spectrum
was made from all detected electrons, irrespective if ions where detected in coincidence or not. We will refer to these two peaks simply as peak A and peak B. Despite the fact that the Auger decay inevitably leads to doubly charged final states, the contribution of doubly charged ionic fragments to the pattern of fragmentation is small. Therefore it is clear, that ion pair production is the dominating process. As shown in figure 2 the patterns of fragmentation of the ions vary depending if the ions are found in coincidence with electrons from the F-site or the CH$_{3}$-site. Some of the ions, e.g. F$^{-}$ (19 amu) only appear after ionization of the F-side, others like F$_{3}$Si-CH$_{2}$-CH$_{2}^{+}$ (117 amu) are exclusively produced after ionization on the CH$_{3}$ side. A quantitative measure of the site selectivity is the asymmetry defined as: asymmetry = $(a-b)/(a+b)$. Here $a$ is the number of mass selected ions found in coincidence with electrons in peak A divided by the area of peak A. The range of the asymmetry is -1 to 1. Where -1 means a production exclusively after CH$_{3}$-site ionization, 0 stands for equal chance to get the ion, no matter which Si atom was core ionized, 1 stands for exclusive production after F-site ionization. An analogous definition can be used for ion pairs. In figure 3 the asymmetries for some selected fragments produced after ionization of F$_{3}$Si-CH$_{2}$-CH$_{2}$-Si(CH$_{3}$)$_{3}$, F$_{3}$Si-CH$_{2}$-Si(CH$_{3}$)$_{3}$, and Cl$_{3}$Si-Si(CH$_{3}$)$_{3}$ are shown.

![Figure 3. The observed asymmetries for some fragments for three different target molecules.](image-url)

When one looks at the SiF, SiF$_{2}^{+}$ and SiF$_{3}^{+}$ (SiCl, SiCl$_{2}^{+}$ and SiCl$_{3}^{+}$) fragments, for all three molecules the asymmetry shows a trend from positive to negative asymmetry values. The positive values for SiF$^{-}$ and SiF$_{2}^{+}$ are easy to understand: these fragments belong to multiple bond breaks around the core ionized Si atom on the F-side. The negative asymmetry value of SiF$_{3}^{+}$ means that it is unlikely to get this fragment after core ionization on the F-site, because this leads preferentially to Si-F bond breaks. Instead SiF$_{3}^{+}$ is produced in a bond break reaction happening after Si core ionization on the CH$_{3}$-site. This already shows that bond breaking can also happen far away from the original core hole. We conclude that in general bond break can happen not only next to the core excited atom. However, we will show below that such “non-local” bond break depends on the chemical environment of the core hole. Using the ion pair information is very helpful to understand the details of the fragmentation reaction. By looking at specific ion pairs, e.g. (F$_{3}$Si-CH$_{2}$-CH$_{2}^{+}$, Si(CH$_{3}$)$_{3}^{+}$) one can focus to single bond break reactions whereas the detection of F$_{3}$Si-CH$_{2}$-CH$_{2}^{+}$ or Si(CH$_{3}$)$_{3}^{+}$ without the partner ion, includes multiple bond break reactions as well. It turns out that many such single-bond break reactions do in fact happen close to the core hole site. For the pair (F$_{3}$Si-CH$_{2}$-CH$_{2}^{+}$, Si(CH$_{3}$)$_{3}^{+}$) an asymmetry value of exactly -1 was found i.e. this pair is produced after Si core ionization on the CH$_{3}$-site only. The amount of data is too large to be shown in detail in this paper. Here we only summarize
the most important results: for F$_3$Si-CH$_2$-CH$_2$-Si(CH$_3$)$_3$ ionization of the F-site always leads to the break of both Si-C bonds, while ionization on the CH$_3$-site can keep the Si-C bond on the F-side intact. One may speculate that this phenomenon is connected with the larger number of degrees of freedom for the nuclear motion on the Si(CH$_3$)$_3$ side. So nuclear motion due to core ionization can be absorbed locally. On the other hand the nuclear motion triggered by the Si core ionization is expected to be small [6]. A completely different approach for explaining the distant Si-C bond break after core ionization on the F-side is based on the strong electronegativity of F. Double ionization within the SiF$_3$ part is energetically not favorable, therefore it is likely that electrons from the CH$_2$-CH$_2$-Si(CH$_3$)$_3$ part will be attracted towards the doubly charged SiF$_3$ part leading to bond break within CH$_2$-CH$_2$-Si(CH$_3$)$_3$, i.e. potentially C-Si bond break on the CH$_3$-site. Using the strong electronegativity of F as the basis for the explanation is consistent with other findings that will be presented here. Such an explanation goes clearly beyond the original idea of localized bond breaking as it involves the correlated motion of many electrons throughout the molecule.

4 Molecular size effects in site specific fragmentation

Comparing the results found for F$_3$Si-CH$_2$-CH$_2$-Si(CH$_3$)$_3$ with those for the smaller molecules F$_3$Si-CH$_2$-Si(CH$_3$)$_3$ and Cl$_3$Si-Si(CH$_3$)$_3$ we see the influence of the molecular size. A systematic reduction of the asymmetry values was observed, when the size of the molecule is reduced. This is shown in figure 3 for some selected fragments. The same systematic reduction was found for the asymmetry values for ion pair production. We conclude that in general bond break happens not only next to the core excited atom but can involve at least the bonds one atom away - potentially more. With this rule of thumb it is easy to understand why in earlier experiments using small molecules like N$_2$O [8] the absolute values for asymmetries observed in the partial ion yield where always below 0.5.

5 Nuclear motion

The effects of nuclear motion before the Auger decay can be studied in detail, using the AEPIPICO method. Here the AEPIPICO results for CH$_3$F will be presented. Also for this measurement the photon energies where chosen to lead to core ionization followed by normal Auger decay leading to doubly charged ionic final states, i.e. mainly pairs of singly charged ions. Photon energies of 370eV and 725eV were used and the corresponding dominating ionization processes where C1s and F1s ionization respectively. This experiment was performed to study the effects of nuclear motion on the ion production. Therefore we will compare the experimental findings with the predictions based on the simple model, which neglects the nuclear motion prior to the Auger decay. After the Auger decay the core hole is filled, so within this model the only difference between the C KVV and the F KVV Auger final states is the kinetic energy of the Auger electron, while the eigenstates of the doubly ionized molecule are exactly the same - only the population probabilities i.e. the line strengths differ due to the different overlaps of the core orbital with the relevant valence orbitals. In this description ionic dissociation starting with the same ionic eigenstates - the one corresponding to the same line in the Auger electron spectrum - must inevitably lead to the same branching ratios for the production of pairs of ionic fragments. So if a single electronic state is resolved in an AEPIPICO experiment the probability to get a specific ion pair in coincidence with the Auger electron must be the same for the C1s and the F1s ionization. Within this model the differences in the branching ratios for the partial ion yields or specific ion pair yields for the C1s and F1s ionization are explained only by the different relative strengths of Auger lines for the two core holes. In figure 4 the Auger electron spectra are plotted on an double ionization potential energy scale compensating for the difference of the C1s and F1s binding energies. By selecting only electrons detected in coincidence with a specific ion pair the number of electronic states contributing to the electron spectrum is reduced and the interpretation
becomes much easier. Figures showing the spectra of Auger electrons detected in coincidence with any of the 14 most abundant ion pairs can be found in reference [9] along with the figures for the corresponding branching ratios of the yields as a function of Auger electron energy. It turns out that for most ion pairs the branching ratios as a function of the double ionization potential are quite similar for the C 1s and F 1s Auger decay, suggesting that the above stated model is a good approximation and that either only a single electronic state contributed or that the non-resolved electronic states lead to similar patterns of fragmentation.

![Graph](image)

**Figure 4.** a) and b) The C KVV and F KVV Auger electron spectra of CH₃F. The upper two panels show conventional electron spectra (solid triangles) and spectra of electrons found in coincidence with ion pairs (open triangles). The vertical bars correspond to the double hole final states from reference [10]. c) and d) show the branching ratios to specific ion pairs (H⁺,CF⁻) and (CH₃⁺, F⁻).

There are two interesting exceptions (H⁺,CF⁻) and (CH₃⁺, F⁻). The branching ratios for these two pairs are very different for the C 1s and F 1s Auger decay, as shown in figure 4c and 4d. The behavior of (H⁺,CF⁻) can be explained within the theoretical calculation of reference [10]. In the region 40-50eV there are a number of states associated with the C-H bond breaking. These lines energetically overlap with other lines leading to different ion pairs. As their relative contribution is different for the two core holes, the change in the branching ratio is understandable. However for the (CH₃⁺, F⁻) pair we do not have states with such properties in the energy region 40-50eV. The observed site specific production of this pair is not understandable within the theoretical description based on transitions in the Franck Condon region. We claim that the nuclear motion is the key to understand the (CH₃⁺, F⁻) production and its site specificity. Again the chemical intuition that F attracts electrons is important. Initially a CH₃F⁺ ion is produced. Because of the electronegativity of the F the positive charge is mainly localized on the CH₃ part. If a small stretching of the C-F distance happens before the Auger decay, this is a deviation from the FC region leading to contributions from other double
holes states to the spectrum. Additionally the larger C-F distance explains why the CH$_3^+$ ion can stay intact when an Auger decay within the F atom takes place.

6 Electron transfer reactions

The importance of nuclear motion for the ion production is most clearly demonstrated in the last example we present. Irradiating CH$_3$F with soft x-rays of a photon energy of 688 eV a F1s electron can be excited to an anti-bonding 6a$_1^*$ orbital. This triggers ultrafast dissociation [12]. As the first step is excitation and not ionization the Auger decay will lead to singly charged final ionic states. Therefore electron-ion coincidence spectroscopy is sufficient to analyze the process in detail. The ultrafast fragmentation happens on a similar time scale like the Auger decay. So this is a showcase example for the influence of the nuclear motion on the ion production. A configuration interaction calculation shows that these bands are associated with Auger decay to electronic states that asymptotically yield F$^+$ when the C-F distance is stretched [12]. Assuming an atomic-like Auger decay within F would produce a F$^+$ ion in the vicinity of a neutral CH$_3$. Our experimental data and calculations point towards a more complicated process: the F KVV Auger decay is followed by electron transfer from CH$_3$ to F$^+$. The important experimental detail is the resolution of the Doppler shift arising form the fast motion of the F atom with respect to the electron detector. In an electron-ion coincidence experiment this normally yields the trivial result, that the electron kinetic energy is higher when the F$^+$ ion produced was emitted in the direction of the electron detector and vice versa. The ions that are emitted towards the electron spectrometer need to be bent back towards the ion detector and therefore have to longer times of flight than the ones emitted towards the ion detector. The ion times of flight are labeled “late” and “early” in figures 5 and 6 accordingly. Looking at the coincidences with the F$^+$ ions we see two peaks. A detailed configuration interaction calculation of the core excited state and the Auger final states provides us with a large set of potential curves for the spectator states. The uppermost two curves belong to vertical transition energies labeled S5 and S4 in figures 5 and 6. The spectrum of electron detected in coincidence with CH$_3^+$ ions is very similar to that of electrons detected in coincidence with F$^+$ ions, implying that both belong to the same electronic final states. We
analyzed the correlation of the Doppler shift with the momenta of the F⁺ and the CH₂⁺ ions: therefore we plotted the spectra of electrons that belong to late and early F⁺ or CH₂⁺ ions separately in the upper halves of figures 5 and 6. The Doppler shifts have the same size but opposite sign, indicating that the Auger electron was emitted from F atom and later an electron was transferred from CH₃ to F⁺ [13].

We conclude that electron redistribution towards the F side is a general phenomenon in the ionization and fragmentation of F-containing molecules.

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