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Electron–ion coincidence spectroscopy of a large organic molecule: photofragmentation of avobenzone after valence and core ionisation

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Abstract
The Avobenzone (AVOB) molecule is very photoactive and undergoes irreversible degradation upon irradiation. We studied its valence and core-level (C1s and O1s) photoionisation and subsequent photofragmentation with photoelectron spectroscopy and photoelectron–photoion–photoion coincidence (PEPIPICO) spectroscopy. AVOB is one of the largest molecules studied with this technique. The results show that the AVOB molecule dissociates into an extensive range of fragments by different pathways with little element or site-selectivity. The coincident maps were used to determine selected fragment separation sequences by analysing the slopes of patterns from ion pairs after the core ionisation. Charge delocalisation over the benzene rings and their relative stability favor fragmentation by cleavage of the bridge between them.

Keywords: PEPICO, photofragmentation, time-of-flight mass spectrometry, radiation damage, electron spectroscopy, avobenzone

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction
The photostability of organic molecules is of multidisciplinary interest relating e.g. to radiation damage in biotissues, fragmentation of molecules in the atmosphere, and degradation of UV-absorbers in sunscreens. Ionisation-induced dissociation has been studied with various experimental techniques, including electrospray ionisation [1, 2], ion- and electron bombardment [3–5], and photoionisation [6–8]. With synchrotron radiation (SR), the incident photon energy can be selectively tuned to probe the dissociation dynamics of different photoionised (e.g. valence and core-ionisation) and resonantly excited states [9, 10]. Energy selective analysis is made possible by simultaneous detection of photoelectrons and photoions in coincidence (PEPICO, PEPICO) [11]. In several recent studies PEPICO has been applied to gain insight into the fragmentation dynamics of various molecular systems.
in dicaticonic states (both organic and inorganic). Lindgren et al [12] described the preservation of the molecular alignment of ammonia during many-body dissociation. Ha et al [13] studied the photofragmentation of DNA and RNA sugars. Inhester et al [14] described the lack of site-specificity linked to the population of the same final dicaticonic electronic states after Auger decay. Itālā et al [15] described the suppression of NO production by methylation, on valence ionisation of nitroimidazoles. Levola et al [16] reported site effective photofragmentation of chloro- and bromoacetic acid by utilising core-level ionisation.

In this work, we applied the PEPI(PIC)O technique to study a large organic molecule with two bridged benzene rings, AVOB, also known as butylmethoxydibenzoylmethane. AVOB exists as both enol and keto tautomers, as shown in Figure 1. In solutions, the enol form dominates over the keto form, and the enol–keto ratios are solvent dependent [17, 18]. Upon exposure to UV radiation, the enol form changes to the keto form [19], a process called enol–keto tautomerisation. An equilibrium between enol and keto forms cannot be reached because of the efficient generation of the keto triplet excited state via which the molecule dissociates [19]. The AVOB keto form in triplet state can also interact with surrounding molecules and triple–triplet energy or electron transfer processes can occur [20]. AVOB is one of the most frequently used organic UVA filters, and various studies have been performed on its tautomerisation and photostability. In Abid et al [19], UV-driven irreversible photodegradation of the solvated molecule was seen with the help of chromatography and transient absorption spectroscopy. Photodegradation by UV radiation was studied by Alfonso et al [21]. Dunkelberger et al [22] and Verma et al [23] defined mechanisms of the photoionisation. Roscher et al [24] explained the photodecomposition mechanism. Lhiaubet-Vallet et al [25] and Cantrell et al [26] explained the formation of a reactive triplet state that leads to singlet quenching. Recently, Berenbeim et al [27] studied the tautomer dependent degradation of the AVOB molecule with infrared radiation.

Here, we extend the photofragmentation studies of AVOB to the VUV and soft X-ray range and explore the formation of charged radicals upon valence and core-level ionisation of the molecule in gas-phase. At valence level, we report near-threshold time-of-flight (TOF) mass spectra and PEPICO measurements, giving approximate appearance energies of different fragments. For C1s and O1s core-levels, we report photoelectron spectra (PES) and PEPICO measurements. As the complex molecule can fragment in a multitude of ways and the charge separation can take place at different points of the decay pathway, we have evaluated different scenarios and predicted the slopes of the C1s PIPICO patterns based on a simple model of momentum conservation [7, 28, 29]. Comparison between the modeled and experimentally observed slopes allow us to single out some fragmentation mechanisms even in the case of such a large molecule as AVOB (310 amu).

2. Methods

2.1. Experimental methods

The experiment was performed at the newly built FinEst-BeAMS (Finnish–Estonian Beamline for Atmospheric and Material Science) beamline at MAX IV synchrotron facility, Sweden [30]. FinEstBeAMS is located at the 1.5 GeV ring of MAX IV, and it has two branches, one dedicated to solid-state experiments, while the other hosting the gas-phase endstation (GPES), on which we performed our experiments. The GPES has an electron–ion coincidence setup, consisting of a Scienta R4000 hemispherical electron analyser equipped with a fast position-sensitive detector, and a momentum-imaging multi-hit capable ion TOF spectrometer [31]. The AVOB sample was purchased from Cayman Chemical (Ann Arbor, MI, USA) with a purity of ≥ 98%. An effusive gas beam of AVOB molecules was generated using a resistively heated oven maintained at a steady temperature slightly above 100°C. Heat induced decomposition to thermal ions was excluded by measuring TOF mass spectra without SR excitation, where no ions were observed. However, thermal decomposition for neutral fragments was not monitored.

The measurements were performed at the magic angle of 55°. In this experiment, the TOF spectrometer was operated in the Wiley–McLaren mode [32, 33], to detect positive ions created upon ionisation. Appearance energies of fragments were studied in the photon energy interval 7.5–10 eV, using a MgF2 window to reduce the intensity of higher-order light [30]. The PEPICO and PEPIPICO measurements corresponding to valence, C1s, and O1s photoionisation were performed at 70 eV, 350 eV, and 599 eV photon energy respectively, collecting electrons in a kinetic energy range from 55 to 66 eV.
Electron–ion coincidence spectra always contain some ‘false’ coincidences that do not originate from the same molecular ionisation event. To reduce the appearances of false coincidences, the count rate was lowered to about 10 to 20 real electron counts/s. The data analysis was carried out using CoboldPC (Roentdek Handels GmbH, Germany) software, and plotted with the help of the OriginPro program (OriginLab Corp., MA, USA). The TOF spectra were calibrated using the water and AVOB parent ion as reference peaks. C1s and O1s electron binding energies were calibrated by introducing carbon dioxide gas to the experimental chamber as a reference for the electron detector was operated in ‘fixed-detector signal to kinetic energy, because during the coincidence experiment the electron detector was operated in ‘fixed-mode’, necessitating the dispersion calibration. The binding energy of valence PES was calibrated with reference to the 1b1 water peak at 12.62 eV [37].

2.2. Computational methods

In order to gain insight which of the isomers our gas-phase experiment was probing, molecular ab initio calculations were carried out with the GAMESS code [38–40]. The optimised gas-phase geometries of a related molecule, 4-methoxy-dibenzoylmethane, were selected as a starting point for both the keto and chelated enol tautomers [41]. The geometry of the whole AVOB molecule was then optimised by attaching a tert-butyl group to the rest of the molecule with different starting geometries. Due to the size of the molecule, the geometry optimisation was only feasible at the restricted (open-shell) Hartree–Fock (ROHF) level of theory [42], using a Dunning-type correlation consistent cc-pVDZ basis set for all the atoms [43], as implemented in the GAMESS code. Using the ROHF-level optimised neutral ground-state geometries, single-point energy calculations were performed for the neutral and singly ionised keto and chelated enol tautomers, using Møller–Plesset 2nd order perturbation theory (MP2) [44–46]. The calculations were carried out at 0 K.

3. Results and discussion

3.1. Calculations

In accordance with the results obtained by Kojić et al [41], the total energy of the gas-phase keto tautomer was found to be lower than that of the chelated enol tautomer. The optimised geometries can be found from the supplementary material (https://stacks.iop.org/JPB/53/244001/mmedia). The energy difference between these tautomers was found to be 47 meV at the MP2 level of theory. Based on Maxwell–Boltzmann statistics, at 100 °C the occupation of an energy level with 47 meV higher energy is only approximately 20%, suggesting that the keto tautomer should be more abundant in gas-phase according to the calculations. Similar results were obtained by Berenbeim et al [27] for protonated AVOB. This would suggest that the keto tautomer would be the more stable one in the gas-phase. However, given the small energy difference and limited accuracy of the model, based on only the total energy we cannot conclude that the keto tautomer would be the one we have probed in this gas-phase experiment. In order to get more insight to the binding energy differences between the tautomers that are observable using photoelectron spectroscopy, we calculated the vertical ionisation energies (VIE) and used orbital energies to form model PES to which experimental ones were compared. VIE were 8.27 eV and 7.93 eV for the keto and chelated enol tautomers, respectively, the latter value agreeing better with the observed VIE of 8.0 eV. The use of orbital energies to model PES is of course a very crude model of photoionisation, neglecting all the relaxation and electron correlation effects. However, regardless of their simplicity, they proved to be very useful and predicted the shape of the PES relatively accurately. The O1s orbital energies of the C=O and C–O–C/C–OH groups are well separated and their intensity ratios vary from 2:1 in keto form to 1:2 in chelated enol form. Thus, based on comparison of the modeled and experimental O1s PES, we conclude that the chelated enol tautomer is dominating in our experiment. The presence of the keto form in minor quantity cannot be excluded. The comparison of the calculated and experimental valence, C1s, and O1s PES is presented in the following sections.

3.2. Valence ionisation

Figure 2(a) shows the TOF mass spectra of the AVOB molecule recorded for several photon energies, ranging from 7.5 to 10.0 eV. The parent ion and its heavy fragment with 284 amu start to appear above 7.5 eV (the adiabatic ionisation threshold is estimated to be 7.6 eV from PEPICO). When the photon energy is higher than 9.0 eV, fragments with masses less than 200 amu start to appear. Until 10 eV photon energy, most of the fragments of AVOB have appeared. Figure 2(b) shows a TOF mass spectrum recorded with 70 eV photon energy in coincidence with electrons in binding energy range from 6 to 15 eV, which is lower than the double ionisation energy, thus limiting the ions to those produced by single valence ionisation.

Some residual H2O, O2, and N2 molecules were observed at 70 eV photon energy. 10 eV photon energy is below the ionisation energies of these residues and they thus do not contribute to figure 2(a), where most of the fragments are from AVOB molecules (some contribution of impurities are also observed at masses 322 and 335 amu). Thus, in addition to the N2 molecule, the CO-fragment of AVOB contributes to the 28 amu peak.

Table 1 shows the detailed breakdown of the TOF mass spectrum of outermost valence ionisation, recorded with 70 eV photons and in coincidence with 6–15 eV binding energy electrons. As visible in figure 2 and quantified in table 1, the relative fragment yields differ between the 10 eV and 70 eV measurements. With 10 eV photon energy, only the outermost molecular orbitals can be ionised, while in the 70 eV coincident experiment final states up to 15 eV binding energy were collected, as shown in figure 2(c). According to the molecular calculations, the outermost molecular orbitals with orbital energies <10 eV are located in the benzene ring, in both keto and chelated enol tautomers. The orbital energies
Figure 2. (a) The TOF mass spectra measured at photon energies from 7.5 to 10.0 eV with a step of a 0.5 eV. (b) TOF spectrum of ions measured in coincidence with electrons in the binding energy range 6–15 eV, recorded at 70 eV photon energy. Masses of some prominent peaks and their respective mass-to-charge ratios are indicated. (c) Valence PES at 70 eV photon energy. Black colour with unfilled circles shows the total PES in coincidence with all ions, all other colours are PES in coincidence with a specific ion, as indicated in the legend. The solid black and dashed red spectra with offsets are calculated spectra of chelated enol and keto tautomers, respectively.

of the molecular orbitals located in the keto-groups or OH-group are above 10 eV, and in the experimental photoelectron spectrum a broad band indeed starts at 10 eV.

The coincident valence photoelectron spectrum is shown in figure 2(c). The all-electron spectrum is shown in black colour, all other curves in different colours are PES in coincidence with different fragment ions. The black and dashed red solid lines with vertical offsets are calculated valence spectra for the enol and keto tautomers, respectively. They were obtained by convolution of the calculated orbital energies with 0.5 eV Gaussian and 0.1 eV Lorentzian for better visualisation. The valence PES has two main characteristic regions. The shape of the lower binding energy region (<10 eV) agrees quite well with the calculated enol spectrum, but just judging from the shape of the modeled valence PES, we cannot exclude the possibility of both isomers being present in the gas-phase. Most fragments start to appear already when these outermost orbitals are ionised, but the detected ions are mostly the parent ion and that of a mass 135 amu. The non-coincident mass spectrum recorded at 10 eV photon energy gives very different abundances for the ions than the 70 eV coincident experiment in the binding energy region below 10 eV. For example, apart from the parent ion, the most abundant ion is 284 amu at \( h\nu = 10 \text{ eV} \), while this ion has much lower intensity in the binding energy region <10 eV compared to e.g. the 135 or 108 amu ions in figure 2(c). This indicates that there is a strong photon energy dependence in the photoionisation of outermost orbitals, and it is possible that near-threshold resonances modify the fragmentation pattern.

In the higher binding energy region (>10 eV), relative abundancies of different fragments change quite drastically as a function of binding energy. For example, non-dissociative ionisation decreases above 12 eV binding energy, when production of \([\text{M} - \text{CH}_3]^+\) (295 amu) increases. The
133–136 amu fragments are clearly abundant already when the
outermost orbitals are ionised, but their production notably
increases when molecular orbitals related to the ‘bridge’
between benzene rings are ionised above 10.5 eV. The yield
of 107–108 amu fragments (benzene ring + OCH$_2$) increases
above 12 eV, when orbitals located at the methoxy and tert-
butyl groups are accessed. Besides this, the valence electron
spectrum also has a significant contribution from the resid-
ual H$_2$O signal, but this can be effectively filtered out by the
PEPICO method, as seen in figure 2(c).

### 3.3. C1s ionisation

The coincident core–shell C1s PES in the binding energy
range from 287 eV to 295 eV recorded with 350 eV photon
energy is presented in figure 3(a). The total C1s PES is shown
in black colour, all other lines in different colours are PES in
coincidence with selected fragment ions. Coincident ion PES
have been normalised by dividing the intensity by the inte-
rated intensity (area) of the total PES. The C1s PES has two
main peaks from the different chemical environments. Accord-
ing to the model calculations, the higher binding energy peak
at 292.1 eV corresponds to ionisation from the C=O and C–O
sites, and the lower binding energy peak at 290.0 eV to ioni-
sation from the alkyl groups and benzene rings. The binding
energy ordering of these functional groups is in agreement with
observations from other molecules containing similar groups
[47]. Many ionisation sites with slightly different chemical
environments broaden the C–C, C–H peak, and ionisation-
induced vibrations [48] can contribute to the asymmetric peak
shape on the higher binding energy side.

The breakdown of the total C1s PES to contributions from
different fragments reveals some site-selectivity. Lighter
charged fragments (15 amu and 27–29 amu) are relatively
more abundant, when the C–O sites are ionised, compared to
ionisation from C–C sites. Ionisation from the alkyl and aryl
sites produce slightly more charged 133–135 amu fragments
than ionisation from the C–O sites. Another way to study the
site-selectivity is to divide the C1s PES into three different
regions and to look at the TOF mass spectra obtained in coin-
dence with electrons from these specific regions (figure 3(b)).
The higher binding energy peak is included in region 1, and the
large lower binding energy peak was divided into the regions
2 and 3, as indicated in figure 3(a). The different TOF mass spe-
ctra in figure 3(b) were normalised by setting the intensity of the
highest intensity peak, corresponding to 77 amu, to one. At
first glance, the TOF spectra of each region look very similar,
except for some minor differences. The peaks at 27 and 29 amu
look like a doublet formed by CO$^+$ ion (28 amu) having such
a large kinetic energy release (KER), that only ions emitted
toward and opposite to the detector are detected. This inter-
pretation is not fully supported by the image of the position dis-
tribution of the ions, since counts are not uniformly distributed
over the detector, but more counts are observed in the middle
part. The alternative assignment for these peaks are C$_2$H$_5^+$
(27 amu) and C$_2$H$_7$/COH$^+$ (29 amu). The 29 amu ion seems to
be slightly more abundant in coincidence with electrons in region
1. Similarly, there is an indication of a doublet peak (39 to 41
amu), which could originate from large kinetic energy frag-
ments C$_7$O$^+$ or C$_9$H$_7^+$. Alternatively, this range could have a
contribution from a series of C$_m$H$_n$($m = 1$–5) and/or C$_3$OH$^+$
($n = 0$–2). The most striking difference between the regions
is the very sharp peak at approximately 147 amu, which is the
most abundant in region 3. The calculated molecular orbital
energies indicate that apart from the benzene ring the tert-butyl

### Table 1. Detailed breakdown of valence ionisation fragments and their relative yields with respect to the parent ion at 10 eV (non-coincident) and 70 eV (in coincidence with 6 to 15 eV BE) photon energies, corresponding to the TOF mass spectra shown in figures 2(a) and (b). For peaks that show additional structure, a range of number of hydrogen atoms is given.

| Mass (amu) | Chemical formula | Ion yield 10 eV | Ion yield 70 eV | Mass (amu) | Chemical formula | Ion yield 10 eV | Ion yield 70 eV |
|------------|------------------|----------------|----------------|------------|------------------|----------------|----------------|
| 14         | N$^+$            | 0.01           |                | 107        | C$_7$OH$_2^+$    | 0.05           |                |
| 15         | CH$_3^+$         | 0.01           |                | 108        | C$_8$O$_2$H$_4^+$| 0.30           |                |
| 16         | O$^+$            | 0.02           | 114–123        | C$_6$OH$_4^+$ or C$_6$H$_4^+$ | 0.005 | 0.24 |
| 17         | OH$^+$           | 0.05           | 133            |            |                  |                |                |
| 18         | H$_2$O$^+$       | 0.73           | 135            | C$_6$O$_2$H$_7^+$ | 0.022 | 0.50 |
| 28         | N$_2$/CO$^+$     | 0.10           | 143–149        | C$_5$O$_2$H$_6^+$ (n = 3–9) | 0.010 | 0.16 |
| 31         | CO$_3$H$_3^+$    | 0.05           | 161            | C$_7$OH$_3^+$ | 0.049 | 0.21 |
| 32         | O$_2^+$          | 0.10           | 177            | C$_8$O$_2$H$_5^+$ | 0.010 | 0.09 |
| 39         | C$_2$H$_3^+$     | 0.03           | 186            | C$_9$OH$_4^+$ | 0.04 | 0.04 |
| 41         | C$_2$OH$_1^+$    | 0.05           | 203            | C$_9$O$_2$H$_5^+$ | 0.03 |                |
| 44         | CO$_2^+$         | 0.02           | 233            | C$_9$O$_2$H$_7^+$ | 0.007 | 0.07 |
| 50–54      | C$_2$H$_4^+$ (n = 2–6) | 0.03 | 267 | C$_9$O$_2$H$_5^+$ | 0.007 | 0.05 |
| 57         | C$_2$H$_4^+$     | 0.06           | 284            | C$_9$O$_2$H$_5^+$ | 0.047 | 0.05 |
| 62–65      | C$_2$H$_4^+$ (n = 2–5) | 0.08 | 295 | C$_9$O$_2$H$_5^+$ | 0.004 | 0.30 |
| 69         | C$_5$H$_3^+$     | 0.15           | 310            | C$_9$O$_2$H$_5^+$ | 1.000 | 1.00 |
| 77         | C$_3$H$_4^+$     | 0.11           | 322            | Impurity | 0.003 | 0.02 |
| 91–92      | C$_6$OH$_5^+$ (n = 3–4) | 0.13 | 335 | Impurity | 0.020 | 0.04 |
group especially contributes to this region. The ion around 147 amu is interpreted as a stable doubly charged parent that has lost CH$_3$. The interpretation is further confirmed by the analysis of ion–ion coincidences, where the 147 amu fragment was not found to be coincident with any other ion, and its position distribution is concentrated in the middle of the ion detector. Other sharp TOF peaks showing counts tightly concentrated in the middle of the detector were observed at non-integer masses around 118, 120, 134 amu, which can also be doubly charged ions. They are overlapping with broad features of different shapes which in turn were created in decays with significant KER. The different number of hydrogen atoms in the fragments also broaden the observed TOF peaks. The ion at 69 amu, which can be associated with C–C–(CH$_3$)$_3^+$, stands out as being a clearly sharper feature than the neighbouring peaks.

### 3.4. O1s ionisation

Figure 4(a) shows the coincident core–shell electron spectrum in the binding energy range from 533.5 to 544 eV, recorded with 599 eV photon energy. The O1s total PES is shown in black colour, all other peaks in different colours are PES in coincidence with different fragment ions. The calculated orbital energies convoluted with 1 eV Gaussian and 0.2 eV Lorentzian shapes of the enol and keto forms are shown as black and dashed red solid lines with offset, respectively. The O1s PES also has two main peaks arising from the different chemical environments. The small peak towards the lower binding energy side at 536.1 eV is due to ionisation in the C=O site. The broad larger peak around 538.5 eV is due to ionisation in the C–O–C, and C–OH sites in the enol form. In addition, the O1s PES shows a significant contribution from the residual H$_2$O, as seen in figure 4(a). By comparing the experimental and calculated electron spectra, it is clear that the enol form of the AVOB molecule is dominating over the keto form. There are also some signs of site-selectivity, observed after the breakdown of the total O1s PES into contributions recorded in coincidence with different fragments. For example, the CH$_3^+$ fragment (15 amu), the CO$_2^+$ fragments (ranges from 27–29 amu), and the 118 amu fragment exhibit similar intensities within region 1, but the filtered PES of 25–31 amu fragments has clearly higher intensity in region 2. This means that when the C–O–C–OH site is ionised, fragmentation produces more CO$_2^+$ related fragments, but when the C=O site is ionised, all these fragments are produced with equal probability. Similarly, slight site-selectivity is observed when fragments with 69 amu and 133–135 amu are compared; within the region 2, the PES related to 69 amu fragment has higher intensity than the PES of 133–135 amu fragments, whereas the opposite is true in region 1. The small increase of intensity around 541.5 eV binding energy in the PES of 25–31 amu fragments is probably due to the presence of some leftover CO$_2$ calibrant gas in the chamber.

Unlike the C1s PES, the O1s PES is also divided into two different regions and the TOF mass spectra obtained in coincidence with electrons from these specific sites are presented in figure 4(b). The TOF mass spectra are normalised by setting the highest intensity peak (77 amu) to one. The TOF spectra of
Figure 4. (a) The O1s PES measured at 599 eV photon energy, the black line with unfilled circles indicates the all electron spectrum, lines with different colours are PES in coincidence with specific mass peaks from TOF mass spectra. The solid black and dashed red spectra with offsets show the calculated PES of the enol and keto tautomers, respectively. (b) TOF mass spectra measured in coincidence with O1s photoelectrons from regions 1 and 2 as indicated in (a).

different regions are very similar to each other, and also similar to C1s ionisation. Again, a sharp peak at 147 amu is observed with some site-specificity, as in the case of C1s ionisation. The comparison of C1s and O1s TOF mass spectra is presented in the supplementary material.

3.5. C1s PEPIPICO maps

After core-level ionisation, the molecule undergoes an Auger decay, primarily leaving the molecule doubly ionised. Triply ionised final states can also be produced via additional shake-off type processes during the Auger decay, or via double Auger decay, but such processes are much less probable compared to normal Auger decay. Using a predictive formula by Roos et al. [49], and assuming that only valence electrons from the nearest neighbouring atoms can participate in the decay, in average the probability for triply ionised states is about 10% for both core-level ionisation. This is supported by the fact that no significant correlation between two first ions and the third ion was found, indicating that events with three or more ions mostly result from false coincidences. Thus, we only concentrate on normal Auger decay here, and assume that the contribution of triply ionised states for the ion-ion coincidences is small.

PEPIPICO maps are one of the best techniques to study fragmentation in multi-ionisation processes; a more detailed description of the technique and analysis can be found e.g. in [50]. In short, in the PEPIPICO map (figure 5) the TOF of the faster ion is on the x-axis, and the TOF of the slower ion is on the y-axis. The cation pairs originating from the same fragmentation process showed up on the PEPIPICO map as tilted ‘cigar-shaped islands’, due to the isotropic initial velocity and momentum correlation of ion pairs [51]. The cation pairs are catagorised as two-body, three-body, and many-body dissociation, depending on how the doubly charged nascent parent ion dissociates. Every different fragmentation island on the PEPIPICO map represents a different fragmentation mechanism or pathway, but sometimes the same pair can be produced in several ways, and the island thus consists of two or more overlapping islands.

AVOB is one of the heaviest molecules studied by PEPIPICO spectroscopy until now. The doubly charged parent ions dissociate into many different fragments, because the charge separation is quite efficient, followed by several different further fragmentations. Most of the doubly charged ions seem to be highly unstable, and the energy is released via dissociation into different singly charged and neutral species. The daughter cations created from the same ionisation event are correlated to each other and share the KER. After core ionisation, different fragments up to 177 amu are observed, which indicates the AVOB molecule to be more stable than other heavy molecules studied before, like thymidine [6], or d-ribose [13].

Fragmentation of AVOB does not proceed through simple bond cleavage only, but also by different rearrangements such as McLafferty rearrangements [52] and elimination processes take place during fragmentation. Those are observed during the fragmentation of the organic molecule in the keto group, when the beta-cleavage is proceeded by the gain of $\gamma$-hydrogen [53, 54]. Berenbeim et al. [27] recently proposed the presence
Figure 5. (a) Full PEPIPICO map of AVOB after Cls ionisation. The PEPIPICO map is further divided into three different regions, A, B, and C. (b) The enlarged PEPIPICO map of region C. The red boxes in the map show discussed coincident pairs, and vertical and horizontal lines show the specific mass on both axes.

Table 2. The selected coincident pairs with indication of mechanisms, slope analysis, and relative yield.

| Coincident pair | Fragment 1     | Fragment 2     | Mechanisms | Experimental slope | Calculated slope | Ion-pairs per 1000 counts |
|-----------------|----------------|----------------|------------|--------------------|------------------|--------------------------|
| (118, 135)     | C9H+           | C9O2H+         | a          | −0.9               | −1.0             | 20                       |
| (107, 133)     | C10H+          | C8O2H+         | c          | −0.9               | −1.0             | 10                       |
| (118, 177)     | C10H+          | C9O2H+         | d          | −1.0               | −1.1 or −1.0     | 5                        |
| (135, 160)     | C10H+          | C11O3H+        | e          | −1.0               | −0.9 or −1.0     | 4                        |
| (133, 135)     | C10H+          | C9O2H+         | f          | −0.9               | −1.3             | 12                       |
| (92, 118)      | C6H+           | C9H+           | g          | −1.6               | −1.7             | 27                       |
| (69, 118)      | C5H+           | C9H+           | g          | −2.2               | −2.3             | 14                       |
| (69, 135)      | C5H+           | C8O2H+         | h          | −1.7               | −2.5             | 4                        |
| (77, 118)      | C5H+           | C9O2H+         | i          | −1.2               | −1.3             | 31                       |

of McLafferty and ring walk-in elimination rearrangements with similar fragments by multi-photon dissociation of the gas-phase AVOB molecule, as we also observed in our measured mass spectrum.

The PEPIPICO map of AVOB after Cls ionisation (hv = 350 eV) is shown in figure 5. From the first look of the coincidence map, the light fragments are seen in the PEPIPICO map as broad ‘islands’ of counts without a clear slope. There is a contribution from false coincidences to these islands, but the unclear slope patterns are mostly due to release of neutral fragments decreasing the momentum correlation between the two ions. This was already observed for thymidine [6] and uridine [55]. Most of the islands in the PEPIPICO maps after Cls ionisation are due to many-body dissociation processes.

Figure 5(a) shows the map divided into three different sub-regions. In figure 5(b), some thought-provoking coincident ion pairs are indicated and their calculated and experimental slopes and relative yields are given in table 2.

For sequential dissociation, it is possible to do a slope analysis as described in [7, 29]. Every ion has a TOF $T \pm \Delta T$, where $T$ is the nominal TOF (without initial kinetic energy), and $\Delta T$ depends on the velocity and direction of the ion after fragmentation. In this slope analysis model, it is assumed that the kinetic energy of neutral fragments is comparatively small. In the plot, the pattern is defined by the slope ($\Delta T_{\text{max}} / \Delta T_{\text{max}}$), known as the experimental slope. For two-body dissociation, the slope will be $-1 (k = -q_1/q_2$, where $k$ is the slope of the PEPIPICO pattern, and in our case we only considered singly charged fragments, thus $q_1 = q_2$ is the elementary charge). The change in flight time for many-body processes is directly proportional to the mass of the ion so the slope can be estimated from the ratio of the masses (e.g. $M_{\text{ion}} / M_{\text{precursor}}$), which is known as the calculated slope. For further details see for example Simon et al [28] and Itäliä et al [7, 29].

The full PEPIPICO map is divided into three different regions (A, B, and C). The region C mostly consists of the massive charged fragments, as enlarged in figure 5(b). We propose some mechanisms how these pairs may have been created, as shown in figure 6. We did not focus too much on the regions A and B, which mostly consist of smaller fragments and unclear patterns due to many-body dissociation as discussed before. One of the strongest and clearest patterns in the ion-ion coincidence map in figure 5(b) is the coincident pair (118, 135).
Figure 6. The schemes for proposed mechanisms of selected coincident pairs from the PEPIPICO map. CT stands for 'charge transfer'.
It can be produced by at least three different fragmentation mechanisms. Figure 6(a) presents one of them, deferred charge separation, in which the doubly charged parent ion first loses a neutral tert-butyl group, and the charges are separated in the second step of dissociation into two charged fragments (118, 135). This process would give a slope of $-1$. Another option would be that charges are separated in the first step, producing a 135 amu ion, and a 175 amu ion, which further dissociates into 118 amu and 57 amu fragments. In that case, the slope would be $-1.48$ for the ion pair (118, 135), or if the 57 amu fragment is charged, the slope for the (57, 135) pair would be $-3.07$. From the coincidence map, it is clear that the (57, 135) ion pair is much weaker than the (118, 135) pair, and also the observed slope of $-0.9$ for the (118, 135) pair matches the deferred charge separation better. The third option which was considered is presented in figure 6(b). It is a process following the secondary decay in which the charge separation takes place in the first step. The charged fragment of a mass 175 amu further dissociates into a 133 amu and a 42 amu fragments. In this step, the charge can be transferred to a 42 amu or a 133 amu fragment. In the third step, the 133 amu fragment further dissociates into 118 and 15 amu fragments. This mechanism would result in a slope of $-1.5$, which is not observed. Note, that here the 118 amu fragment is different than the one in the deferred mechanisms presented above. Many different possible configurations of the fragments complicate the analysis of the dissociation mechanism, but the above example demonstrates that in some cases where the coincidence pattern is clear, we can propose the mechanism and a configuration for the ion. It should also be noted, that some (42, 135) pairs are observed in figure 5(a), region B, but with a lower intensity than the (118, 135) pair.

The coincident ion pair (107, 133) is produced by secondary decay with many-body dissociation, as seen in figure 6(c). In the first step, the doubly charged parent ion is separated into two singly charged fragments with 135, and 175 amu mass. In the second step, each of these singly charged fragments dissociates further into charged and neutral fragments.

The coincident ion pairs (118, 177) and (135, 160) have the experimental slope of $-1$. They can be produced by simple secondary decay and/or deferred charge separation with three-body dissociation, as presented in figures 6(d) and (e). The slope of $-1$ is produced, if a neutral fragment is lost in the first step and the charge separation takes place in the second step. A slope slightly less or more than $-1$ is obtained, if in the first step the doubly charged ion dissociates into two singly charged fragments, and in the second step one of the charged fragments dissociates into charged and neutral fragments. Whether the slope is more than $-1$ or less than $-1$ depends on whether the dissociating fragment is the heavier or lighter of the ions created at the point of charge separation. Since the secondary decay in this case also gives a slope very close to $-1$, we cannot definitely separate the deferred and secondary decays. For the ion pair (133, 135), the fragmentation mechanism is presented in figure 6(f). Here, only secondary decay is possible, because the neutral fragment is released from the bridge between the benzene rings and accessible only after charge separation in the first step.

The coincident ion pairs (92, 118) and (69, 118) are produced by deferred charge separation followed by secondary decay, as shown in figure 6(g). In the first step, the doubly charged parent ion dissociates into a doubly charged fragment ion with 279 amu, and a neutral fragment with 31 amu. In the second step, charge separation takes place in the doubly charged fragment, resulting in two charged fragments with 118 and 161 amu, respectively. In the third step, the 161 amu charged fragment dissociates into a 92 amu charged fragment and a 69 amu neutral fragment, or the other way around. The charge transfer to either of the fragments is possible, because experimental and calculated slope of both scenarios match well. The coincident pair (69, 135) is proposed to follow secondary decay in three steps.

The coincident pair (77, 118) is one of the most intense ones in the coincidence map. A process which produces a slope which matches the experimental slope quite well is presented in figure 6(i), and follows from deferred charge separation taking place in the third step.

In the depicted fragmentation mechanisms in figure 6, it is evident that charge can be transferred to either heavier or lighter fragments, but it is observed that the production of heavier ions is more probable in these cases. The charge transfer depends on delocalisation efficiency of the charge, which in turn depends on the presence of lone pairs, the number of $\pi$-bonds, and the size of the fragment. In some cases, the experimental slope can be identical with the calculated slope, both for secondary decay and deferred charge separation, which indicates that either of the fragmentation mechanisms would be possible. Many fragments can have different amounts of hydrogen atoms, which makes the PEPIICO patterns unclear. The coincidence patterns may also show a ‘twist’ if we look at them carefully (in supplementary material figures S2 and S3). The twist means that the most intense part of the contour feature has a different slope than the a less intense part, which suggests the presence of concurrent mechanisms, or mechanisms following different dynamics [56, 57].

4. Conclusions

We reported the first gas-phase valence, C1s, and O1s PES of AVOB. Based on model calculations and O1s PES, we conclude that the enol form of AVOB was dominating in this gas-phase experiment. Valence photoionisation results in a rich photon energy dependent fragmentation pattern with fragments in a mass range of 15 to 295 amu, in addition to the parent ion at 310 amu. Valence PEPICO analysis gave insight to changes in the fragmentation when different orbitals get ionised. The outermost valence orbitals are mostly located at the benzene rings, while the orbitals localised around the ‘bridge’ between the rings are accessible only above 10.5 eV.

The core–shell (C1s and O1s) ionisation leads to dissociation of the molecule with ions in the range of 12 to 177 amu, with little site-selectivity ($C=O$ vs. $C–C$, and $C–O$ vs. $C=O$ ionisations) in relative production of fragments. However, the element-selectivity is very small, as the total fragmentation pattern and the relative abundance of the fragments are very similar no matter whether the C1s or the O1s
core-level is ionised. Even after the core-ionisation of AVOB, the benzene rings tend to stay intact, as ions with $m/q > 72$ form a significant fraction from the total yield.

The unstable dicaticonic final states produced via Auger decay after core ionisation display a large number of fragmentation pathways. We observed secondary decay and deferred charge separation mechanisms, that can be followed by further fragmentation. The adequate retention of ion–ion momentum correlation between heavier fragments allowed us to use the sequential model formulated for the slope analysis in literature [7, 28, 29]. Based on the slope analysis, we proposed a reconstruction of sequential dissociation pathways for some heavy ion–ion fragment pairs. These fragmentation mechanisms involve the cleavage of the molecular bridge between the two benzene rings in the charge separation step. During the deferred charge separation process, before the actual charge separation, the neutral fragments leave mostly from the outer arms of the benzene rings. This also indicates that most of the charge is delocalised over the two benzene rings. Several isomeric forms of the fragments can be present, and their structure cannot be resolved in TOF-based ion detection giving only mass-to-charge ratio. Thus, the geometries in the depicted mechanisms are tentative, and further geometrical changes can occur, such as ring-openings.

In the future, coincidence experiments can be extended to Auger electron—fragment ion coincidences. In this way, one can study the fragmentation as a function of final dicaticonic states, which would give interesting insight how the final electronic state and its charge delocalisation affects the fragmentation. As the tautomerisation of AVOB and many other UV-filter molecules can be driven by laser excitation, they offer an interesting platform for pump–probe experiments for example at FELs. The present study provides an overall picture of molecular dissociation of AVOB after valence and core-ionisation, and thus good background for such time-resolved studies.

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