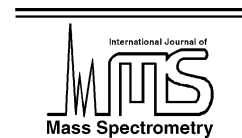




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Fission mechanisms of doubly charged organic molecular clusters

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Abstract

Fission of doubly charged clusters and subsequent stabilization of the singly charged fragments is reported. Specifically, homogeneous clusters containing organic molecules, such as *o*-deuteromethanol (CH₃OD) and benzene (C₆H₆), are investigated. Doubly charged clusters are prepared by core level excitation near the carbon K-edge. The singly charged products are observed by photoelectron–photoion-coincidence (PEPICO) spectroscopy. Correlated pairs of singly charged cations are detected by photoelectron–photoion–photoion-coincidence (PEPIPICO) spectroscopy. This approach allows us to derive fission mechanisms, including kinetic energy releases, and charge separation distances. Specifically, doubly charged CH₃OD clusters decay after fission into deuterated products via an intracuster deuteron transfer. Doubly charged benzene clusters are primarily stabilized via fission and subsequent evaporation of neutrals, similar to rare gas clusters. The results are compared to previous work on the corresponding isolated gas phase species and charge separation in atomic Van der Waals clusters. (Int J Mass Spectrom 220 (2002) 99–110)

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1. Introduction

Multiply charged molecules and clusters are known to be often unstable with respect to fission [1]. The fission process involves charge separation (*Coulomb explosion*), since singly charged products are formed with considerable amounts of recoil energy, which can be well described by a simple point charge model of electrostatic repulsion [2–5]. The stability limits of multiply charged species have been the subject of numerous studies on variable size clusters, where species with sizes below this limit undergo spontaneous fission [1].

Various experimental and theoretical approaches have been developed in the past to investigate doubly or multiply charged species, such as atoms, molecules, or clusters. Electron impact ionization [6], collisions with highly charged ions [7–9], and femtosecond laser radiation [10] are typical experimental approaches, where mostly outer shell electrons are removed from the neutral precursor, so that multiply charged species are formed. In addition, theoretical work on Coulomb explosion of highly charged clusters, their energetics and dynamics has also been performed [11]. Photoionization in the inner valence excitation regime leads to direct double ionization. This is easily accomplished by the use of vacuum ultraviolet line sources, such as He(II)-radiation [3–5] or synchrotron radiation [12]. However, direct double ionization is of low cross

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section, so that alternative approaches, such as core level excitation, are more efficient to produce doubly or multiply charged ions. Moreover, resonant core level excitation via tunable soft- and hard-X-rays provides an efficient way of site- and element-specific excitation and the subsequent formation of doubly or multiply charged clusters [13]. The ionization yield, i.e., the number of holes that is produced per absorbed photon, can be efficiently varied when tunable sources of radiation, such as synchrotron radiation, are employed [14].

The fission products are often detected by mass spectrometry [1], where the fission process yields products of lower charge with considerable amounts of kinetic energy. This approach is not quite specific, especially in excitation regimes, where single ionization is dominant. Thus, coincidence experiments are advantageously applied, since these suppress efficiently the single ionization events [3–5]. The most simple approach is ion–ion-coincidence spectroscopy, where exclusively correlated pairs of cations are detected [15], whereas the single ionization events can only contribute to a background of false coincidences. More sophisticated approaches involve multiple ion detection, or the primary detection of the photoelectron [3–5] or an energy-selected Auger electron [16]. This leads to the selection of processes of interest, so that more specific information is obtained from such studies. Substantial progress in the field of charge separation of doubly charged molecules has been obtained from photoelectron–photoion–photoion coincidence (PEPIPICO) spectroscopy, where not only the correlated cation pairs can be identified, but also the signal shape analysis allows to derive plausible fission mechanisms [3–5]. The slope of the PEPIPICO signals gives detailed information on plausible fission mechanisms. For simple two body dissociation, deferred charge separations, and simultaneous multiparticle formation one observes a slope of -1 . On the other hand, signal slopes different from -1 are determined by the mass ratio of the stable cation that is observed by mass spectrometry and the unstable intermediate cation that is produced by fission. Moreover, the signal width along the slope gives information on the kinetic energy release of the fission process.

Coincidence approaches have also been applied to free clusters, so that also size-dependent fission mechanisms were derived [17–19]. First experiments concentrated on rare gas clusters and there are also some results on heterogeneous clusters as well as molecular clusters that contain simple diatomic molecules [18]. Later work also included covalent species, such as sulfur clusters [20,21].

We extend this series of studies on free clusters and report in this paper results on fission of core-excited organic Van der Waals clusters. This study follows earlier work, that was exclusively focused on the corresponding isolated species [22,23]. These have been investigated by similar experimental approaches as used for the present work, where mostly inner valence shell excitation was employed. It will be shown in the following that there is more violent fragmentation upon core level excitation. However, this issue is not the central subject of the present paper.

We have chosen clusters of methanol and benzene as typical model systems of organic clusters for the following reasons:

- (i) Methanol clusters represent a typical organic model system with hydrogen bonds. Singly charged methanol clusters are efficiently stabilized via proton transfer, so that protonated molecular and cluster fragments are formed along with the evaporation of neutrals [24]. Similar stabilization routes are known from clusters of other organic compounds, such as aldehydes [25] and amines [26]. Besides the dominant proton transfer, there are other weak product channels [27,28].
- (ii) Benzene clusters are a typical organic Van der Waals system, where the molecular cation is known to be of considerable stability. Singly charged benzene clusters are known to decay preferentially via losses of neutral molecules [29]. Thus, there should be some similarity compared to rare gas clusters, which were investigated in previous work [17–19].

We focus in this study on photoelectron–photoion-coincidences (PEPICO) and PEPIPICO and aim to

derive fission mechanisms, similar to previous work on rare gas clusters [18] and covalent clusters [20].

2. Experimental

The experimental setup has been described earlier in some detail [18,19]. Therefore, we give only a brief description of the major components. Synchrotron radiation is used for excitation of neutral Van der Waals clusters, where the soft X-ray regime was employed ($E \approx 300$ eV). The experiments were performed at the HE-TGM-2 beam line of the electron storage ring BESSY-I (Berlin, Germany) [30]. The photon energies for the experiments were chosen to be above the edge-jump of the carbon K-ionization continuum of the samples under investigation. This gives high sensitivity to the samples of interest and high efficiency in the formation of doubly charged clusters.

The clusters were prepared by adiabatic expansion of gas mixtures, using the seeded beam technique [31]. Helium was used as a seed gas at variable stagnation pressure p_0 , reaching up to $p_0 \sim 3.5$ bar. The samples were kept at room temperature ($T_0 = 300$ K), so that most of the gas phase ($\sim 95\%$) consists of the seed gas, which was expanded through a nozzle ($d = 50$ μm). This approach does not allow us to derive reliable average cluster sizes, as obtained from the expansion of neat atomic or molecular gases because of inefficient cooling of the internal degrees of freedom [32,33]. However, the systematic variation of the expansion conditions and the use of helium as a seed gas already shows, that the size regime that is explored in this study concentrates preferentially on small clusters near the threshold of cluster formation, so that it can be assumed that the clusters contain less than ~ 50 molecules. Moreover, expansions with helium also avoid the formation of heterogeneous clusters (cf. [34]), which is unlike the use of argon as a seed gas [19].

The cluster jet was skimmed by a 500 μm skimmer. It was crossed with the beam of monochromatic soft X-rays in the ionization region of a combination of spectrometers. Cations were extracted to one side into

a time-of-flight mass spectrometer, whereas electrons were detected by a channeltron multiplier, which was mounted opposite to the time-of-flight mass spectrometer. The extraction of the charged particles was accomplished either by pulsed voltages, so that time-of-flight mass spectra were obtained, or by continuous voltages in the coincidence mode. The field strength in the ionization region was typically set to 300 V/cm during the experiments. PEPIICO spectra were measured at constant photon energy in the C 1s-excitation regime, where a multihit time-to-digital converter was used for coincidence data acquisition (MIPSYS, FLY TDC) [19]. The time resolution was typically set to 4 ns. The setup also allows us to measure simultaneously PEPICO spectra as well as photoelectron-photoion-photoion-photoion-coincidences (PEPIPIICO) (cf. [35]).

The samples were of commercial quality. Benzene (C_6H_6) (Aldrich, purity: 99.9%), *o*-deuteromethanol (CH_3OD) (Merck, purity: 99.9%), and helium (Messer Griesheim, purity: 99.996%) were used without further purification.

3. Results and discussion

3.1. Methanol clusters

Fig. 1 shows a PEPICO spectrum of *o*-deuteromethanol ($\text{CH}_3\text{OD} \equiv \text{M}$) clusters. We have chosen the isotope labeled compound instead of methanol (CH_3OH) in order to determine the influence of the different hydrogen sites on chemical fragmentation, that is followed by fission. The excitation energy was set to 289 eV, which corresponds to the C 1s (CH_3) $\rightarrow 3p/\pi_{\text{C-H}}^*$ -transition, according to previous work on inner-shell electron energy loss spectroscopy [36]. Excitation at other photon energies does not change the experimental results that are shown in this section. We note, that the efficiency of the formation of doubly charged species increases in the core ionization continua compared to the pre-edge regime, similar to the ionization yield (cf. [14]). This also implies that triple ionization, which may occur via a double Auger decay, is expected to be weak.

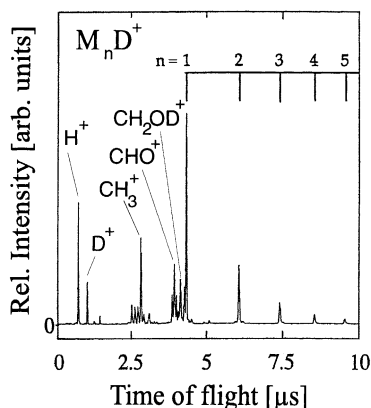


Fig. 1. PEPICO spectrum of *o*-deuteromethanol clusters $[(\text{CH}_3\text{OD})_n \equiv \text{M}_n]$. Experimental conditions: $E = 289 \text{ eV}$; $T_0 = 300 \text{ K}$; $p_0 = 2.4 \text{ bar}$, seed gas: He.

The PEPICO spectrum shows various cation signals, where the low mass regime ($m/z < 33$, corresponding to species that are lighter than the molecular parent cation) is dominated by molecular fragments (see Fig. 1). We also note that C 1s-excitation of the bare molecule yields higher cation intensity for the light mass channels (e.g., H^+) and substantially smaller yields of those cations that are close to the parent cation compared to previous work at 40.8 eV (cf. [37]). This already indicates that fission is dominant in the C 1s-regime leading preferably to smaller fragments than single ionization. As soon as the stagnation pressure p_0 is increased the following changes are observed.

The deuterated parent cation MD^+ occurs with enhanced intensity. This species belongs to a series of cluster cations $(\text{CH}_3\text{OD})_n\text{D}^+$ (M_nD^+) with $n \geq 1$. Such products have also been observed by single ionization [24,28], so that it is not clear how these fragments are formed after core level excitation. Previous work has shown, that these products can be formed from charged clusters via proton transfer [24,28]. This corresponds in the case of CH_3OD -clusters to a deuteron transfer. Thus, the isotope labeled compound clearly shows that the center that is preferably involved in proton transfer belongs to hydroxyl group and not to the methyl group. Thus, isotope scrambling prior to fragmentation can be ruled out (cf. [28]). Similar results have been obtained earlier from selectively deuterated clusters of aldehydes [25]. However, recent work also indicates that another channel involving the methyl group is also present with minor intensity in the singly charged methanol dimer [28]. This leads upon fragmentation to the protonated molecule. Products of more complicated fragmentation from singly charged cluster cations have also been discussed [28]. These are also of minor intensity.

We conclude, that core-excited molecules and clusters yield massive fragmentation compared to outer-shell excitation, but for clusters there are no new product channels compared to earlier photoionization work (cf. [38]) that can exclusively be attributed to fission of doubly charged clusters.

Further insight into fission is obtained from PEPICO spectra. Fig. 2 shows an overview spectrum,

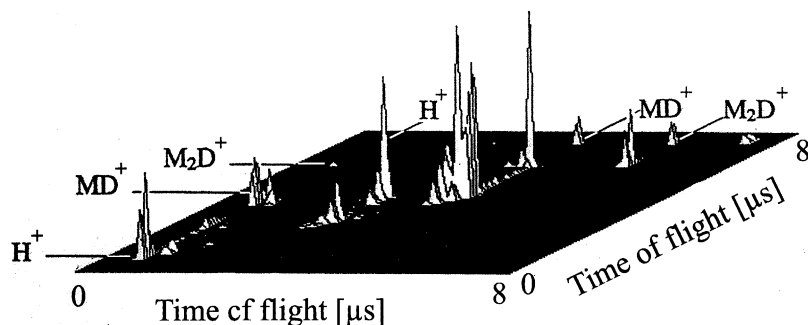


Fig. 2. PEPICO spectrum of *o*-deuteromethanol clusters $[(\text{CH}_3\text{OD})_n \equiv \text{M}_n]$. Experimental conditions: $E = 289 \text{ eV}$; $T_0 = 300 \text{ K}$; $p_0 = 2.4 \text{ bar}$, seed gas: He.

where both the molecular and cluster fission regime is shown. Systematic studies indicate upon changes of the stagnation pressure (p_0), that products channels which are due to fission of doubly charged clusters increase as soon as p_0 is enhanced. The PEPIPICO spectrum of methanol and the fission mechanisms have been reported earlier [22]. We will therefore not include this part of the spectrum in the discussion. We note that the PEPIPICO spectrum of the bare C 1s-excited molecule is dominated by cation pairs, where either H^+ or D^+ are the lighter moiety. The relative intensities of the observed fission channels that come exclusively from clusters are compiled in Table 1. It is found that fission of clusters does not only lead to singly charged deuterated fragments, but there are also molecular fragments, such as CH_3^+ , CHO^+ , and CH_2OD^+ , that are correlated with cluster cations. They are already observed at moderate stagnation pressure ($p_0 \approx 1$ bar) with higher intensity than at increased p_0 . This indicates that such fission channels

come preferentially from small clusters, whereas cation pairs containing exclusively deuterated cluster cations dominate at higher p_0 , i.e., they result from fission of larger clusters. The latter fission channels reach at $p_0 = 1$ bar $\sim 26\%$ of the fission intensity, whereas a fraction of $\sim 45\%$ is observed at $p_0 = 2.4$ bar. We also note that the fraction of the symmetric fission products is almost constant and accounts for $\sim 40\%$ of the total charge separation intensity. This fraction is regarded to be an upper bound for the symmetric fission channels, because some of the cation pair intensity may contain some artifacts that result from autostop signals near the main diagonal ($t_1 \approx t_2$) of the PEPIPICO spectrum (see Fig. 2). This can easily occur when one cation pulse produces two stop signals. The experiments were optimized, so that this quantity is as small as possible, but the results show that the asymmetric fission channels are dominant, similar to previous work on rare gas clusters [18].

We will discuss in the following the four most dominant asymmetric fission channels in greater detail. We use for the analysis of the PEPIPICO shapes contour plots and evaluate the signal slope, yielding fission mechanisms, and the width of the signal, which corresponds to the kinetic energy release of the recoil ions [3–5,20,22]. The results are compiled in Table 2.

The fission channel CH_3^+/MD^+ (with $M = CH_3OD$), shown in Fig. 3(a), occurs primarily in the small cluster regime, i.e., at low p_0 (cf. Table 1). Therefore, it is not surprising that the fission mechanism, that is deduced from the PEPIPICO shape, starts with a trimer dication (see Table 2). However, we note that the PEPIPICO approach cannot give evidence, whether there is evaporation of neutrals prior to fission. After fission both singly charged cations, M^+ and M_2^+ , undergo further stabilization, yielding the correlated products CH_3^+/MD^+ . Thus, the slope of the PEPIPICO signal is governed by the competing processes of stabilization of both singly charged intermediates $M^+ + M_2^+$. Fragmentation of the methanol cation into $CH_3^+ + OD$ is expected to occur with high efficiency, since this route yields more stable products than the alternative route, where the charge is located on the other fragment (i.e., $OD^+ + CH_3$).

Table 1

Intensity of correlated cation pairs, as obtained from PEPIPICO spectra at $E = 289$ eV excitation energy of CH_3OD -clusters (M_n) (without molecular contributions), $T_0 = 300$ K, seed gas: He. The intensities are only considered for those clusters up to M_3D^+ (with $M = CH_3OD$)

Cation pair	Relative intensity at $p_0 = 1$ bar (%)	Relative intensity at $p_0 = 2.4$ bar (%)
H^+/MD^+	1.3	1.6
CH_3^+/CH_3^+	11.4	5.1
CH_3^+/CHO^+	3.1	1.6
CH_3^+/CH_2OD^+	3.6	2.8
CH_3^+/MD^+	15.1	13.0
CH_3^+/M_2D^+	–	1.4
CHO^+/CHO^+	5.1	3.1
CHO^+/CH_2OD^+	7.3	4.3
CHO^+/MD^+	6.9	5.3
CH_2OD^+/CH_2OD^+	3.3	2.4
CH_2OD^+/MD^+	16.8	14.1
MD^+/MD^+	23.6	25.3
MD^+/M_2D^+	1.6	9.6
MD^+/M_3D^+	–	2.4
M_2D^+/M_2D^+	0.9	4.4
M_2D^+/M_3D^+	–	2.0
M_3D^+/M_3D^+	–	1.6

There is also cation intensity above this mass channel with considerably lower intensity.

Table 2
Fission mechanisms in CH₃OD-clusters

Process	Calculated slope according to process	Experimental slope of the PEPIPICO signal	Kinetic energy release (eV)	Charge separation distance (Å)
Fig. 3(a)	-1.17	-1.20 ± 0.05	2.9 ± 0.5	5.0 ± 1.0
I. Fission $M_3^{++} \rightarrow M_2^+ + M^+$				
II. Secondary decay $M^+ \rightarrow \underline{CH_3^+} + OD$ $M_2^+ \rightarrow \underline{MD^+} + (M-D)$				
Fig. 3(b)	-0.60	-0.60 ± 0.05	2.3 ± 0.3	6.3 ± 0.9
I. Fission $M_3^{++} \rightarrow M_2^+ + M^+$				
II. Secondary decay $M^+ \rightarrow \underline{CHO^+} + 2H + D$ $M_2^+ \rightarrow \underline{MD^+} + (M-D)$				
Fig. 3(c)	-0.73	-0.70 ± 0.05	3.1 ± 0.5	4.6 ± 0.9
I. Fission $M_5^{++} \rightarrow M_3^+ + M_2^+$				
II. Secondary decay $M_2^+ \rightarrow \underline{CH_2OD^+} + M + H$ $M_3^+ \rightarrow \underline{MD^+} + M + (M-D)$				
Fig. 3(d)	-1.46	-1.50 ± 0.05	2.1 ± 0.5	6.9 ± 2.1
I. Fission $M_7^{++} \rightarrow M_4^+ + M_3^+$				
II. Secondary decay $M_3^+ \rightarrow \underline{MD^+} + M + (M-D)$ $M_4^+ \rightarrow \underline{M_2D^+} + M + (M-D)$				

The results are deduced from Fig. 3(a–d). The observed correlated cation pairs are underlined. See text for further details.

On the other hand, the dimer cation is stabilized via a deuteron transfer yielding MD⁺. The contour plot shown in Fig. 3(a) also contains with weak intensity the signature of a protonated molecule (MH⁺), which is correlated with CH₃⁺. This is evidently due to the weak channel, which involves the methyl group for the proton transfer, according to recent work on photoionization of the methanol dimer [28], assuming that isotope scrambling is of no importance. The kinetic energy release (KER) is obtained from the signal length perpendicular to the main diagonal of the PEPIPICO spectrum, similar to PIPICO spectroscopy [22]. We obtain a KER of 2.9 ± 0.5 eV, which corresponds to a charge separation distance of 5.0 ± 1.0 Å, if a simple electrostatic point charge model is applied,

corresponding to Coulomb explosion. The KER is by about a factor of 2 smaller compared to fission of the bare molecule [22]. This can be rationalized in terms of intermolecular fission, where the charges are separated on different molecular sites. The distance between two molecules in solid methanol of ~4 Å [39] is similar to the charge separation distance.

This result is rationalized as follows: core level excitation of clusters is accompanied by primary excitation, which is strongly localized. The core hole is created at one atom in a molecule, which undergoes photoionization and relaxation, so that it can be expected that both positive charges are initially located in the valence shell of the excited molecule. This is true, if the Auger electron is emitted into

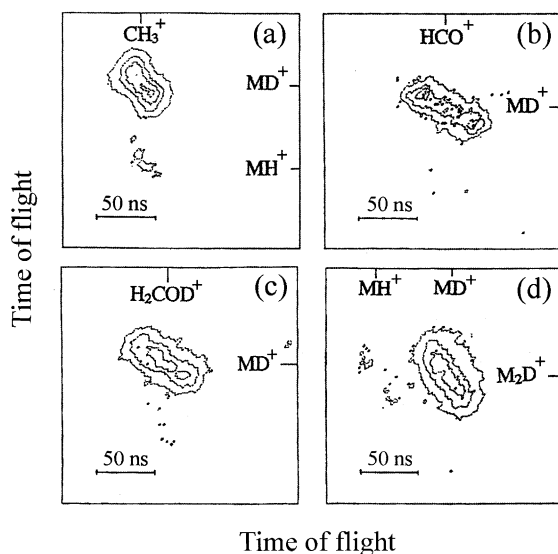


Fig. 3. Contour plots obtained from the PEPICO spectrum of *o*-deuteromethanol clusters $[(\text{CH}_3\text{OD})_n \equiv \text{M}_n]$. Experimental conditions: $E = 289 \text{ eV}$; $T_0 = 300 \text{ K}$; $p_0 = 2.4 \text{ bar}$, seed gas: He: (a) $\text{CH}_3^+/\text{MD}^+$ -region; (b) CHO^+/MD^+ -region; (c) $\text{CH}_2\text{OD}^+/\text{MD}^+$ -region; (d) $\text{MD}^+/\text{M}_2\text{D}^+$ -region.

the vacuum. Alternatively, the Auger electron may hit a neighboring molecule, so that this induces ionization of that molecule. In this case both charges are readily de-localized on different molecules in the cluster. Previous work on solid rare gases indicates, however, that the probability of this process is of the order of $\sim 18\%$ [40,41]. Similar findings are expected to occur for free clusters. In the first case, where both charges are located at the same molecule, other mechanisms of charge de-localization must be active before intermolecular fission can take place. This issue has recently been addressed for weakly bound heteroclusters, where two mechanisms were considered: (i) electron transfer mediated decay and (ii) interatomic/intermolecular Coulombic decay [42]. The results show that the latter process, corresponding to an energy transfer from relaxation of the core hole to the neighboring molecule, leads to charge de-localization. The process dominates at typical intermolecular distances. In contrast, the first process, corresponding to a charge transfer, becomes more

dominant at decreased internuclear separation. We conclude that charge de-localization prior to fission and subsequent fragmentation of the singly charged cations as well as electron impact ionization by the Auger electron fully explain the initial charge separation on different molecules. Subsequently fission and fragmentation of the singly charged intermediates can occur, so that finally the experimentally observed cation pairs are formed.

Fig. 3(b) shows the contour plot of the CHO^+/MD^+ -channel. The slope of the signal is compatible with a mechanism, which is similar to the fission process discussed above, yielding $\text{CH}_3^+/\text{MD}^+$ (see above). The first step after charge delocalization leads to fission, whereas subsequent fragmentation yields the observed cation pair (cf. Table 2). This process also decreases in relative intensity as soon as the expansion conditions favor the formation of larger clusters (cf. Table 1). The experimental kinetic energy release corresponds to $2.3 \pm 0.3 \text{ eV}$ with a charge separation distance of $6.3 \pm 0.9 \text{ \AA}$. These values are also similar to the other process that is discussed above. The results also indicate that the same doubly charged precursors decay into different product channels.

The cation pair $\text{CH}_2\text{OD}^+/\text{MD}^+$ is more efficiently formed at enhanced stagnation pressure (cf. Table 1 and Fig. 3(c)). Consistently, the fission mechanism can be explained by at least a doubly charged pentamer (M_5^{++}) as a suitable precursor (see Table 2). The signal width corresponds to a KER of $3.1 \pm 0.5 \text{ eV}$, or as charge separation distance of $4.6 \pm 0.9 \text{ \AA}$. This is similar to the other channels discussed above, indicating that the maximum KER is obtained, if both charges are located on neighboring molecules.

Finally, we discuss the $\text{MD}^+/\text{M}_2\text{D}^+$ -coincidence signal (cf. Table 1 and Fig. 3(d)). This cation pair gains substantially intensity as soon as p_0 is increased. The signal slope also indicates that there is a primary fission process, where the cluster dication is split into two singly charged cations. Both fragments decay subsequently via deuteron transfer by the loss of one neutral molecule and the corresponding neutral radical ($\text{CH}_3\text{O} \equiv \text{M}-\text{D}$), yielding a pair of

deuterated fragments (cf. Table 2). There is a weak signal that is due to the protonated molecule, but this is of spurious intensity (cf. Fig. 3(d)), which results from fragmentation involving the methyl group.

The KER of the $\text{MD}^+/\text{M}_2\text{D}^+$ -channel is somewhat lower than in the other channels and the charge separation distance consequently higher (cf. Table 2). It is therefore, possible that the smallest neutral cluster, that can be used to rationalize the slope of the PEPICO signal shown in Fig. 3(d), is M_7^{++} . As a result, the minimum charge separation distance is in this case not limited to the nearest neighbor distance. The shape analysis also points to the fact that most of the products are formed with considerably less KER. The shape of the coincidence-signal perpendicular to the main diagonal is found to be somewhat different from the other channels. This indicates that a considerable fraction of the product cation pairs have a much smaller KER than 2.1 eV, corresponding to the maximum KER, which is consistent with large charge separation distances. These can only occur in clusters of sufficient size.

Finally, we note that the doubly charged clusters, which are considered in Table 2 correspond to the smallest cluster that can explain the experimental slopes of the PEPICO signals including the highest KER and the smallest charge separation distance. These results also indicate that the initial fission process is fairly symmetric, yielding intermediate singly charged products of similar mass, which are subsequently stabilized by fragmentation and evaporation. This is unlike fission from doubly charged rare gas clusters, where charge separation gives rise to highly asymmetric channels and evaporation of neutrals only occurs from the larger moieties [18]. The preference to symmetric fission, where cation pairs of the same mass are formed, can also be found from the strong channels that yield products of the same mass. These are not analyzed in this work, since their peak shape can only be recorded to one half near the main diagonal of the PEPICO spectrum, so that there is more ambiguity in the assignment of reliable mechanisms compared to the asymmetric product channels discussed above.

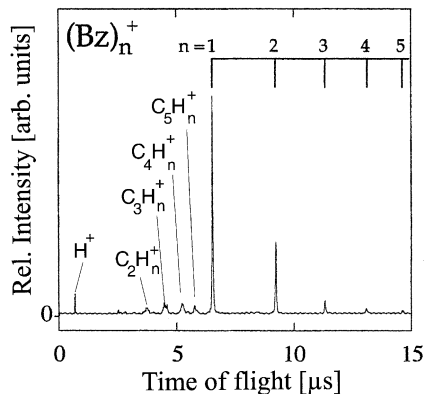


Fig. 4. Photoelectron–photoion-coincidence (PEPICO) spectrum of benzene clusters $[(\text{C}_6\text{H}_6)_n \equiv \text{Bz}_n]^+$. Experimental conditions: $E = 300 \text{ eV}$; $T_0 = 300 \text{ K}$; $p_0 = 3.5 \text{ bar}$, seed gas: He.

3.2. Benzene clusters

Fig. 4 shows PEPICO spectrum of benzene (Bz) clusters. The spectrum was taken at 300 eV excitation energy, which corresponds to the $\text{C } 1s \rightarrow \sigma^*$ -excitation. It is located in the $\text{C } 1s$ -continuum [43,44], where fission is the dominant process. Therefore, the PEPICO reflects efficient fragmentation, rather than direct photoionization of benzene clusters, similar to methanol clusters (see above). This becomes already evident, when the PEPICO of the bare molecules is recorded. It consists of weak intensity near the parent cation C_6H_n^+ (with $n \leq 6$). In contrast, if clusters are present in the jet, the parent cation is the strongest species in the PEPICO spectrum, as shown in Fig. 4. Moreover, all other molecular fragments are weak in intensity. This indicates that the benzene is almost entirely bound in clusters at $p_0 = 3.5 \text{ bar}$, where clustering is considerably stronger than in methanol/helium expansions (see Figs. 1 and 2). This is evidently a result of the considerably lower intermolecular bond energy, which results in less heating of the clusters upon nucleation in the supersaturated gas phase. Efficient cluster formation is well known from previous work on rare gas clusters, where also almost the entire jet was found to consist of variable size clusters [45,46]. Thus, strong PEPICO intensity of benzene cluster cations Bz_n^+ is

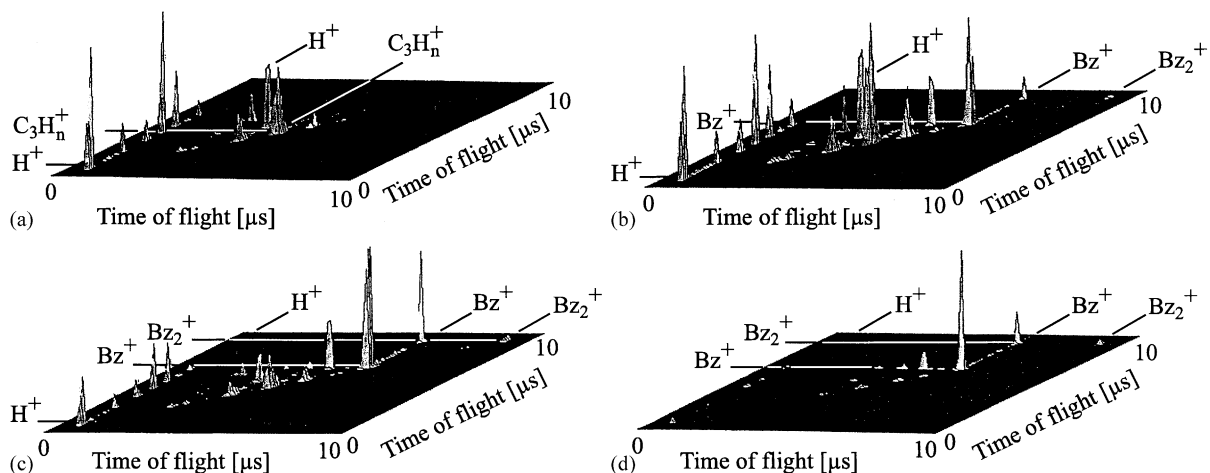


Fig. 5. PEPICO spectrum of benzene clusters $[(C_6H_6)_n \equiv Bz_n]$. Experimental conditions: $E = 300$ eV; $T_0 = 300$ K; seed gas: He: (a) effusive jet of neat benzene; (b) $p_0 = 1.8$ bar; (c) $p_0 = 2.4$ bar; (d) $p_0 = 3.5$ bar.

evidently a result of ionic fragmentation. This comes in the C 1s-regime predominantly from fission, as will be shown in the following. However, PEPICO spectroscopy is not sensitive to distinguish between fission and single ionization, since both processes lead to the same singly charged products [29]. We note that the coincident detection of cluster cations induced by fission of doubly charged clusters is limited by the size regime of unstable dications. In the case of doubly charged benzene clusters Bz_n^{++} the critical size of stable clusters is known to be quite low, corresponding to $n \geq 23$ [47].

Fig. 5 shows a series of PEPICO spectra. These have been recorded at various stagnation pressures p_0 . This varies efficiently the signal ratio between the molecular and the cluster signal. At $p_0 = 1.8$ bar already a quarter of the signal intensity is due to fission of doubly charged clusters (see Fig. 5(b)). This fraction increases to $\sim 50\%$ at $p_0 = 2.4$ bar (cf. Fig. 5(c)). Finally, at $p_0 = 3.5$ bar $\sim 90\%$ of the correlated cation pair signal is due to fission of clusters. The PEPICO spectrum of benzene clusters is dominated by the intense Bz^+/Bz^+ -channel (60%) and with considerably weaker intensity follows the Bz^+/Bz_2^+ -channel (15%). Another coincidence that is due to fission of benzene clusters into $C_4H_n^+/Bz^+$

($n \leq 4$) is also relatively weak (13%) (cf. Fig. 5(d)). The latter cation pair is evidently due to fragmentation of the molecular cation, where neutral acetylene is lost, corresponding to $n = 4$. Such processes are well known from ionic fragmentation of aromatic compounds [48]. It is also possible that more hydrogen gets lost, corresponding to $n < 4$ (see below). This cannot be resolved as a result of the kinetic energy release that accompanies charge separation. Other correlated cation pairs involving Bz^+ along with fragments of the molecular cation are: $C_2H_n^+/Bz^+$ and $C_3H_n^+/Bz^+$. These occur with minor intensity, similar to the Bz_2^+/Bz_2^+ -channel.

Fig. 6 shows contour plots of some selected fission channels from benzene clusters. Fig. 6(a) corresponds to the $C_4H_n^+/Bz^+$ -channel. Its shape is congested, so that an unequivocal slope analysis appears to be difficult. From the central part of the signal, corresponding to $C_4H_3^+/Bz^+$, one would expect a slope of -0.65 , if the unseen neutrals are ejected from an excited benzene cation after fission of Bz_2^{++} . Such slope can indeed be extracted from the experimental contour plot, which give further confidence in the assignment of this decay mechanism. However, the blended signals do not permit an unequivocal assignment of the KER. Perdeuterated benzene may give further clarity

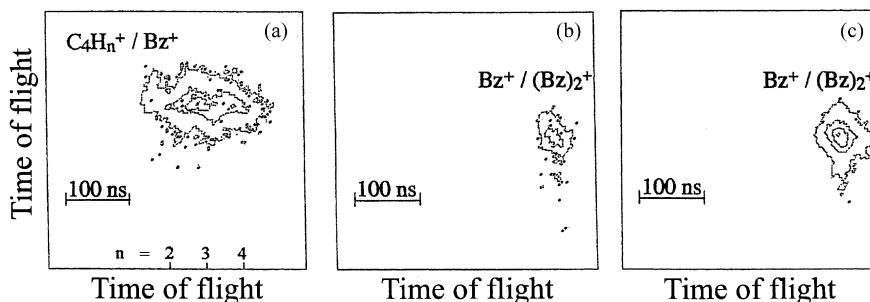


Fig. 6. Contour plots obtained from the PEPICO spectrum of benzene clusters $[(C_6H_6)_n \equiv Bz_n]$. Experimental conditions: $E = 300$ eV; $T_0 = 300$ K, seed gas: He: (a) $C_4H_n^+ / Bz^+$ -region at $p_0 = 2.4$ bar; (b) Bz^+ / Bz_2^+ -region at $p_0 = 1.8$ bar; (c) Bz^+ / Bz_2^+ -region at $p_0 = 2.4$ bar.

on the assignment of the decay mechanisms and the KER.

Fig. 6(b) and (c) show contour plots of the Bz^+ / Bz_2^+ -channel, where Fig. 6(b) has been recorded in the threshold regime of this process ($p_0 = 1.8$ bar). The weak signal has a slope of -1.3 ± 0.1 . This cannot be due to the two body decay of a doubly charged benzene trimer (Bz_3^{++}), where a slope of -1 should occur. The experimental slope of the PEPICO signal rather corresponds to the competing decay of Bz_5^{++} , so that in the first fission step the products Bz_2^+ and Bz_3^+ are formed. Both cations are stabilized via evaporation of a neutral molecule, where the correlated final products Bz^+ / Bz_2^+ are obtained. The calculated slope of this process is -1.33 . If the same products are formed from larger doubly charged clusters involving evaporation of neutrals, then a steeper slope of the order of -1.5 should occur. This is somewhat steeper than the experimental slope that is derived from Fig. 6(b), so that massive evaporation of neutrals after fission is discounted.

Fig. 6(c) shows the contours of the Bz^+ / Bz_2^+ -PEPICO signal at enhanced stagnation pressure ($p_0 = 2.4$ bar). The main signal slope is still identical, but the shape corresponds to a round-shaped diamond. This indicates that the secondary losses contribute considerably to the kinetic energy release relative to the fission of the doubly charged clusters.

The evolution of the Bz^+ / Bz_2^+ -shape as a function of the stagnation pressure shows some similarities

compared to fission in variable size argon clusters [18]. These are also not formed via two body decays in the threshold regime of the PEPICO signals, as evidenced from the Ar^+ / Ar_2^+ -signals [18]. Unlike argon clusters, fission is not as asymmetric in benzene clusters. This already becomes clear, when the signal slopes are compared to those of argon clusters. In this case, one observes that only the heavier cluster cation loses neutrals after fission, whereas the lighter moieties remain intact. In contrast, in benzene clusters evidently both singly charged cations undergo stabilization via evaporation of neutrals.

In the large cluster limit, where the size regime of stable doubly charged cluster is reached, both rare gas clusters and benzene clusters show broad round-shaped PEPICO-signals. In the case of argon clusters this was assigned as evidence for the fact that the momenta of the singly charged products that are formed upon charge separation are not directed into opposite direction, as would be expected for electrostatic repulsion of point charges [18]. We assume that similar processes also occur in doubly charged benzene clusters.

The kinetic energy release, which accompanies the formation of the cation pair Bz^+ / Bz_2^+ is obtained from the coincidence experiments. The largest width of the Bz^+ / Bz_2^+ -signal at $p_0 = 2.4$ bar is 162 ± 10 ns, corresponding to a KER of 2.2 ± 0.2 eV. This corresponds to a charge separation distance of 6.5 ± 0.8 Å. This value is similar to the Bz–Bz-distance, according

to previous work [49], where 4.7 Å were found. Thus, the charges are also delocalized on neighboring molecules, similar to methanol clusters. The maximum KER is given by the intermolecular distance of two molecules. Further charge de-localization can occur, which is found in considerably lower KER near the center of the PEPICO signals.

4. Conclusions

We have investigated fission in molecular clusters containing organics molecules. Two complementary systems are discussed, which are characterized by hydrogen bonds and Van der Waals bonds, respectively. Core level excitation leads to a well localized core hole at one atom, which is bound in a molecule within the clusters. Electronic relaxation leads to two holes in the outer shell, which are stabilized by charge delocalization either via an intermolecular energy transfer or by intra-cluster electron impact ionization of the emitted Auger electron. As a result, the charges can either be delocalized between neighboring molecules in clusters or there is stronger charge separation if the cluster size permits. Rapid charge delocalization evidently suppresses efficiently intramolecular fission in clusters. As a result, the doubly charged clusters undergo various stabilization mechanisms via intermolecular fission and subsequent fragmentation and evaporation of neutrals. The final products are mostly identical to those that are known from single ionization of the clusters, so that there are no dominant product channels, which are exclusively due to fission. This implies that methanol clusters are primarily stabilized after fission via proton (or deuteron) transfer, whereas benzene clusters undergo primarily Van der Waals fragmentation, similar to rare gas clusters [18]. In addition, other fragmentation routes occur in both systems with considerably weaker intensity. Differences to single ionization are primarily found with respect to the kinetic energy release that accompanies fission in doubly charged clusters. The kinetic energy releases are rationalized in terms of the simple electrostatic model of Coulomb explosion.

Charge separation distances are estimated, indicating that these are compatible with structural properties of the clusters and the condensed phase.

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