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Double ionization and dissociation of benzene-d6 induced by collision with H^+ and Ar^{8+}

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Abstract

A 15 keV H^+ or 120 keV Ar^{8+} beam was collided with benzene-d_6 to induce multiple ionization and dissociation. The TOFs of the recoil ions were measured combined with the multiple coincidence technique and the position-sensitive measurement, which allow to identify various dissociation channels and to derive their kinetic energy releases (KERs). By qualitative analysis of TOF coincidence map, it is concluded that in the case of high vibrational excitation, doubly charged parent molecule dissociates into two molecular ions with equal number of carbon atoms in each of them. Comparison of coincidence maps obtained by collisions with H^+ and Ar^{8+} indicates that the number of neutral D-substitution, which were missing from dissociation products, can be used as an indicator of vibrational excitation of parent molecule.

Keywords: Double ionization; Benzene; Dissociation; Coincidence; Position-sensitive

1. Introduction

The stability of multiply ionized molecules depends on their charge states and the sizes. The general trend is that the loss of more electrons makes molecules less stable, and the increase of the molecular size makes the multiply charged molecular ions more stable. In fact, highly charged C_{60} molecules were observed up to 10+ [1], and the availability of highly charged macromolecules makes the mass spectrometric study of biomolecules easier [2], whereas highly charged small molecules generally dissociate very quickly [3].

Benzene is a typical aromatic hydrocarbon and it would be an intermediate case in the sense, that dissociation of the doubly or triply charged benzene would not be very fast, and metastable multiply charged ions of benzene would have some lifetime against dissociation, whereas the dissociation would be still dominant channel. Multiple-ionization of benzene and subsequent dissociation have so far been widely studied by using vacuum UV photons [4], short pulse lasers [5–7], electrons [8], ions [9], and by theoretical calculations [10]. Photoionization study shows that the appearance energies for the fragment ions are considerably higher than those expected for the thermodynamic limits, indicating presence of the large barriers in the dissociation pathways.

In the present study, deuterated benzene molecules were multiply ionized by collision with H^+ or Ar^{8+} and the dissociation scheme of $(C_6D_6)^{2+}$ was examined by utilizing the coincidence measurements of the fragment pairs. The reason to use deuterated benzene instead of benzene was to achieve better mass separation of fragments, differing by only one D. In general, the dissociation pathways can be sorted into following reactions;

$$(C_6D_6)^{2+} \rightarrow C_xD_m{}^+ + C_yD_n{}^+$$
$$(x + y = 6, m + n = 6) \qquad (1)$$

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$$(C_6D_6)^{2+} \rightarrow C_xD_m{}^+ + C_yD_n{}^+ + (6-n-m)D$$
$$(x + y = 6, m + n \leq 5) \tag{2}$$

$$(C_6D_6)^{2+} \rightarrow C_xD_m{}^+ + C_yD_n{}^+$$
$$+(6-x-y)C + (6-n-m)D$$
$$x + y \leq 5, m + n \leq 5) \tag{3}$$

The reaction (1) is two-body dissociation in which coincidence measurement gives information on all the fragments. The reaction (2) includes undetectable neutral fragments, D or D_2, whereas destination of all the carbon atoms can be determined. Reaction (3) includes neutral C and D atoms, thus, includes large unknown factors. Detailed analysis was performed for the reactions (1) and (2).

2. Experimental setup

The projectile H^+ or Ar^{8+} beam, extracted by 15 kV from a 14.25 GHz electron cyclotron resonance (ECR) ion source [11], was electrically chopped to produce 1 kHz pulses with less than 50 ns duration. After chopping, the bunch of ions was collimated by a 0.5-mm diameter pinhole. The diameter of the projectile beam at the collision area was about 1 mm. The target was deuterated benzene (C_6D_6: 99% isotope enrichment), which was used after the conventional degas procedure. The fragment ions produced by collision were extracted by a homogeneous electric field, typically 4.7 V/mm, applied to a 449 mm long drift tube, and were detected by a position sensitive detector (PSD). Details of the TOF spectrometer will be described in the future publication [12]. Details of the PSD working principle are described elsewhere

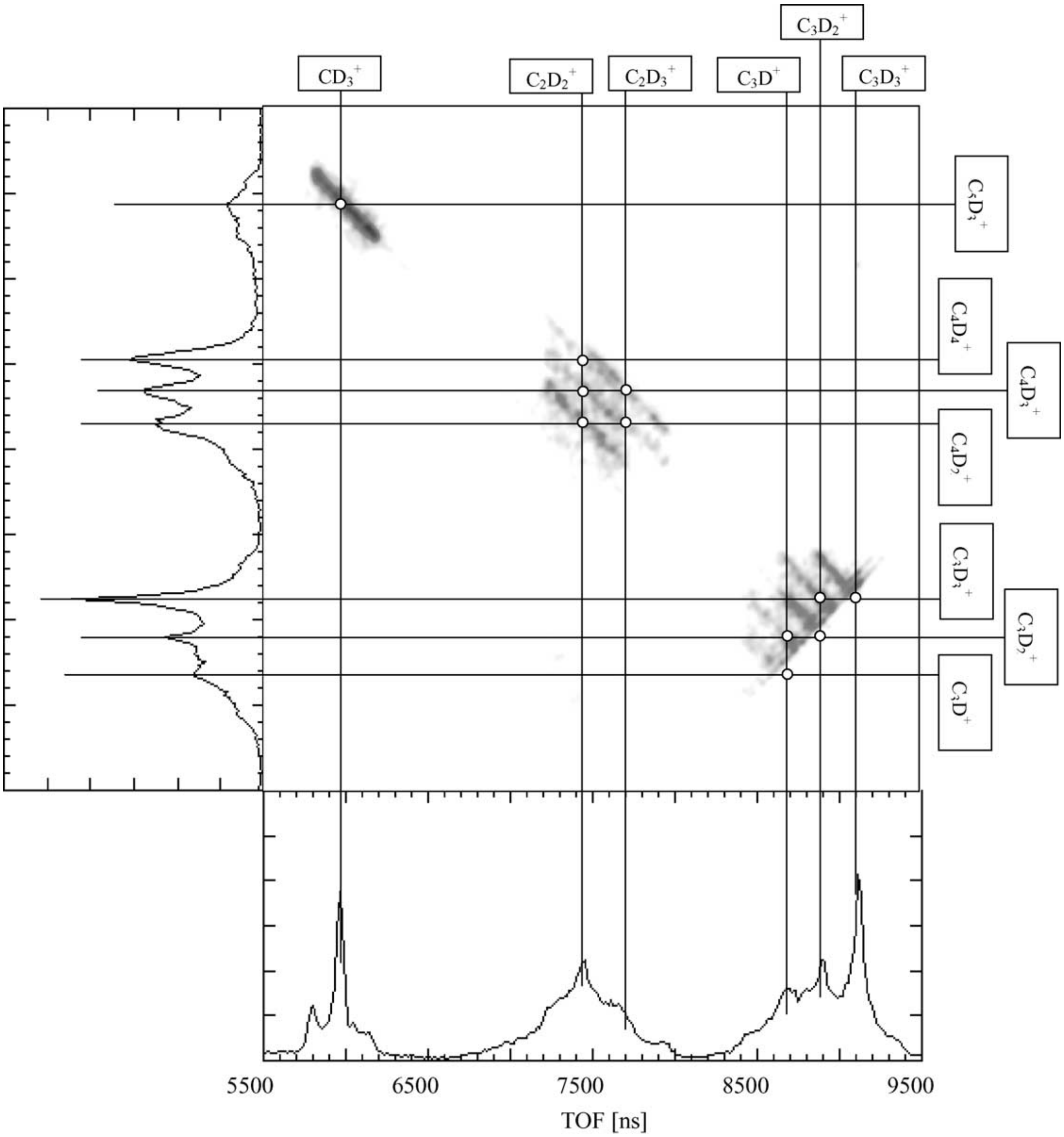

Fig. 1. Double coincidence map relevant to the reactions (1) and (2) (see text). TOF spectrum for all the events (including single-hit) is also shown. The open circles indicate the coincidence of zero-energy fragments. The projectile is H^+.

[13]. As a start trigger we employed the projectile signal from an MCP, placed 600 mm downstream of the collision area.

For the typical value of extraction electric field (4.7 V/mm) and an effective detector diameter of 97 mm ϕ, collection of ions ejected in 4π solid angle was achieved for ion energies up to about 6 eV, which was quite sufficient for our purposes.

3. Results and discussion

Various dissociation channels, corresponding to the reaction (1)–(3), are identified by the double coincidence measurements for the $H^+ + C_6D_6$ collision. Among these coincidence islands, those of $(C_3D_x{}^+ - C_3D_y{}^+)$, $(C_2D_x{}^+ - C_4D_y{}^+)$, $(CD_x{}^+ - C_5D_y{}^+)$ are shown in Fig. 1. Henceforth we will call the group of $(C_xD_m{}^+ - C_yD_n{}^+)$ islands simply as $(C_x{}^+ - C_y{}^+)$ group, so $(C_2{}^+ - C_4{}^+)$ group will mean the group of $(C_2D_x{}^+ - C_4D_y{}^+)$ coincidence islands.

The $(C_3{}^+ - C_3{}^+)$, and $(C_2{}^+ - C_4{}^+)$ groups consist of several lines, each of which corresponds to the different total number of D atoms included in the fragment ions, whereas the $(C^+ - C_5{}^+)$ group consists of the single line, corresponding to the $(CD_3{}^+ - C_5D_3{}^+)$ fragmentation. The numbers of the lost D (hereafter ΔD) in the $(C_3{}^+ - C_3{}^+)$, $(C_2{}^+ - C_4{}^+)$ and $(C^+ - C_5{}^+)$ groups are 0–4, 0–2, and 0, respectively. These coincidence islands are mainly due to dissociation of doubly charged parent, because the sharpness and the linear shape of each island is distinctive characteristic of the two-body dissociation. Comparing the islands with different ΔD, change in the "thickness" of the line-shaped islands can be noticed: lines become thicker for larger ΔD. This is likely to be due to a small (but not negligible) contribution of recoil momentum acquired by fragment ion due to D-loss. The islands for which $\Delta D = 0$ are quite narrow and the islands with different ways of sharing of D but a same way of sharing of C (e.g., the islands $(C_2D_3{}^+ - C_4D_3{}^+)$ and $(C_2D_2{}^+ - C_4D_4{}^+)$) can be discerned.

Concerning the channels with $\Delta D \neq 0$, following molecular fragmentation pathways are possible:

1. $(C_6D_6)^{2+}$ molecule at first undergoes D-loss and then dissociates.
2. $(C_6D_6)^{2+}$ molecule at first dissociates and then the fragment ions undergo D-loss. In such case, initially produced fragment molecular ions would have considerable internal energy.
3. D-loss and ion–ion fragmentation are simultaneous, namely, within a period of molecular vibrations.

In any case, parent $(C_6D_6)^{2+}$ molecule has to be in the highly excited state to induce D-loss, which is most prominent for $(C_3{}^+ - C_3{}^+)$ group. The coexistence of these processes is also possible, depending on the internal energy of the doubly charged parent ions.

Eland and coworkers reported dissociation of doubly charged benzene and argued that the values of KER and branching ratios of the different dissociation channels, involving different total number of H, might be good criteria to differentiate the dissociation mechanisms [4]. If $(C_6D_x)^{2+}$ ion considerably changes the structure depending on the values of x, which might occur for the case 1, then the values of KER will be different for different x. On the other hand, if the D-loss occurs after the ion–ion fragmentation (case 2), then values of KER would be smaller than those of initially formed fragment ions because of the kinematic effect. Under the present experimental conditions, this kinematic effect will be detectable by virtue of the D-substitution.

Fig. 2 shows the plots of KER values calculated for $(C_3D_3{}^+ - C_3D_3{}^+)$ and $(C_3D_1{}^+ - C_3D_1{}^+)$ islands. As can be seen, the peak position of KER distribution is same for $\Delta D = 0$ and $\Delta D = 4$. If the reaction $C_3D_3{}^+ \rightarrow C_3D_1{}^+ + 2D$ occurs, mass number changes from 42 to 38, and thus, about 10% lowering of the KER values is expected. The fact that this is not so, indicates that mechanism 2 is less likely. The cases 1 and 3 appears to be more likely, however, to explain the equal values of the KER for islands with different ΔD, more conclusive evidence is needed.

The large ΔD naturally invokes highly excited parent $(C_6D_6)^{2+}$, and the Fig. 1 indicates that asymmetric fragmentation (asymmetric in carbon sharing) becomes unfavorable as an excitation of $(C_6D_6)^{2+}$ increases. That is, for $\Delta D = 0$, $(C_3{}^+ - C_3{}^+)$, $(C_2{}^+ - C_4{}^+)$ and $(C^+ - C_5{}^+)$ fragmentation processes are all observed, whereas for $\Delta D = 1$–2, $(C^+ - C_5{}^+)$ fragmentation process is not observed, and for $\Delta D = 3$–4, only $(C_3{}^+ - C_3{}^+)$ fragmentation process is observed. It is interesting to note that this fragmentation trend of $(C_6D_6)^{2+}$ is somewhat similar to that of a nuclear fission, where mass sharing between fission products also becomes more and more symmetric as an excitation increases [14]. Concerning the most asymmetric fragmentation, $(C^+ - C_5{}^+)$

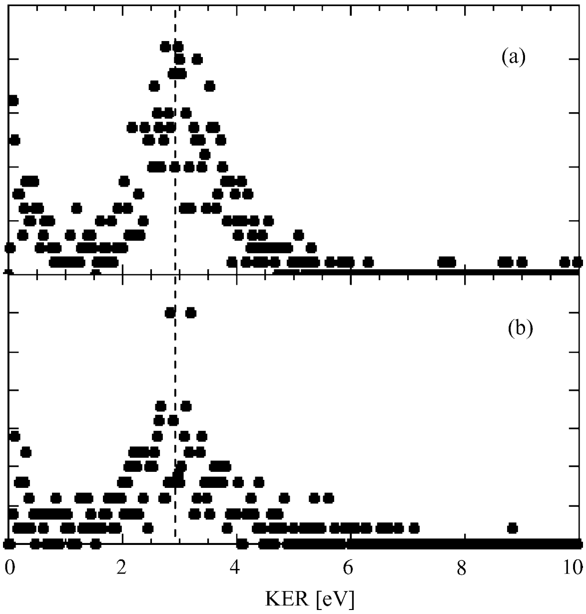

Fig. 2. Plots of the KER values for $(C_3D_3{}^+ - C_3D_3{}^+)$ (a) and $(C_3D_1{}^+ - C_3D_1{}^+)$ (b) islands. Dashed lines indicate peak positions.

process, the sharing of D is exclusively 3 and 3, namely the reaction is

$$(C_6D_6)^{2+} \rightarrow CD_3^{+} + C_5D_3^{+}.$$

This selective reaction channel has been observed in various experiments, and the two-step reaction, a ring-opening reaction associated with D-atom migration followed by fragmentation, is accepted [10]. It is natural to expect that such highly selective reaction would occur at relatively lower excitation energy.

Particularly, interesting is how the excitation depends on the way of ionization. To study ionization/excitation mechanism, an alternative experiment with 120 keV Ar^{8+} as a projectile was conducted. All other experimental settings were same with those for $C_6D_6 + H^+$ collisions. In the case of Ar^{8+} collision, target molecule would be ionized mainly via electron capture by the projectile. Thus, the impact parameter is expected to be much larger, and the vibrational excitation would be associated with the electronic transition, which would be less effective compared to the direct "kick out" by the projectile.

The coincidence map of relevant fragmentation processes obtained by $Ar^{8+} + C_6D_6$ collisions, together with TOF spectrum, is shown in Fig. 3. As can be seen in the figure the maximal ΔD is 2, which is smaller than that obtained by $H^+ + C_6D_6$ collisions. The projectile, on its way out, will interact with produced fragment ions (so called "post collision interaction" or "PCI"), thus, affecting their final velocity vectors. The interaction increases as the charge and the mass of projectile ion increases. This effect can be seen in Fig. 3, in which the coincidence islands are broader than those shown in Fig. 1 (especially prominent for the islands for which $\Delta D = 0$).

Additional feature of vibrational excitation of parent $(C_6D_6)^{2+}$ can be found by comparing KER values of $(CD_3^+ - C_5D_3^+)$ fragmentation channel for H^+ and Ar^{8+}

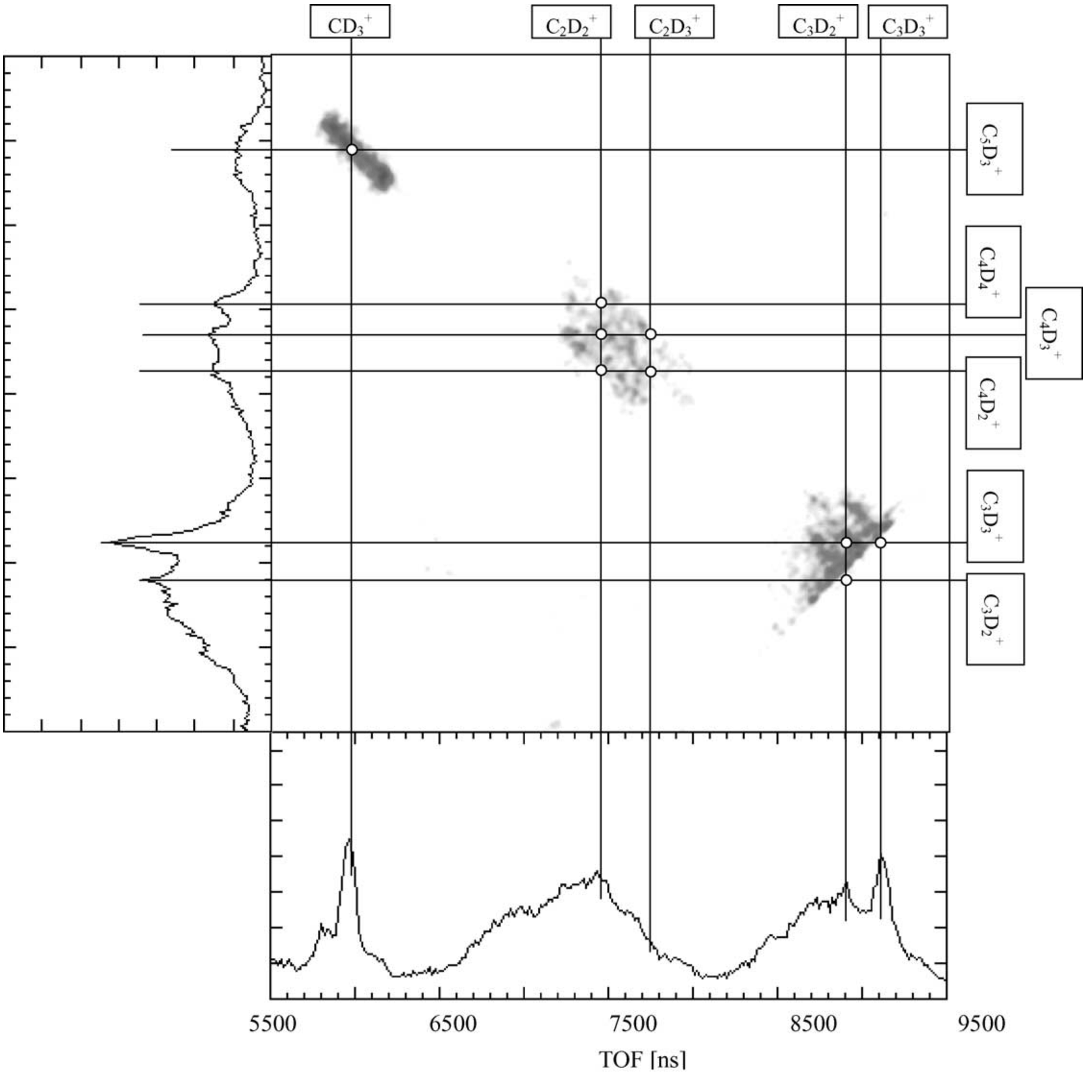

Fig. 3. Coincidence map of molecular fragment ions obtained by Ar^{8+} collisions in the expanded scale. TOF spectrum for all the events (including single-hit) is also shown. The open circles indicate the coincidence of zero-energy fragments.

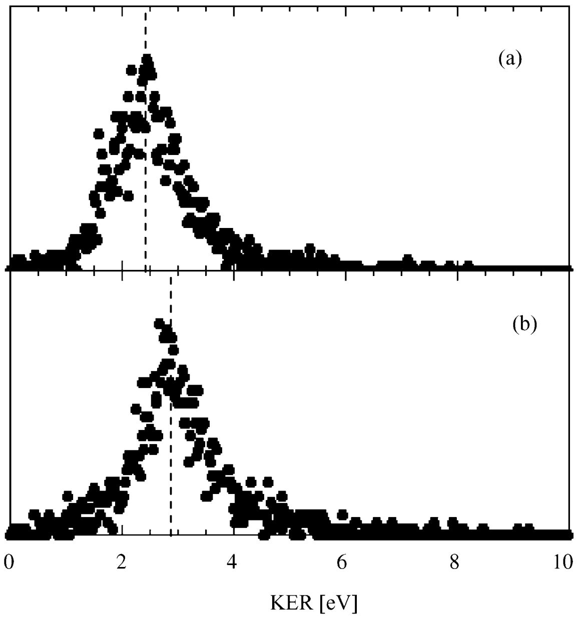

Fig. 4. Plots of the KER values for $(CD_3{}^+ - C_5D_3{}^+)$ island obtained by collisions with H^+ (a) and Ar^{8+} (b). Dashed lines indicate peak positions.

Table 1
Branching ratios and KER values for various coincidence groups from $(C_6D_6)^{2+}$

	H^+		Ar^{8+}		$h\nu$ (40.8 eV) [4]	
	Ratio (%)	KER (eV)	Ratio (%)	KER (eV)	Ratio (%)	KER (eV)
$C^+ + C_5{}^+$	21.6	2.4	21.4	2.8	27.4	3.0
$C_2{}^+ + C_4{}^+$	40.8	2.8	40.6	3.3	37.5	3.8
$C_3{}^+ + C_3{}^+$	37.4	2.9	36.8	3.5	35.0	4.2

projectile cases. Since the vibrational excitation tends to increase the bond lengths in molecule, leading to decrease of Coulomb repulsion between the dissociating ions, it is natural to expect that the increase of the internal temperature of parent ions will be accompanied with decrease of KER values. As can be seen in Fig. 4, the KER value of $(CD_3{}^+ - C_5D_3{}^+)$ island for H^+ projectile is smaller than that for Ar^{8+}; the former peaked at 2.4 eV and the latter leaked at 2.8 eV, again indicating the preferential formation of vibrationaly excited parent by H^+ collisions. This fragmentation channel has also been studied by photoionization, and the peak value of KER was reported to be 3.0 eV [4].

The KER values and relative intensity of different groups is listed in Table 1. Roughly speaking, the trend in the branching ratio is common, $(C_2{}^+ - C_4{}^+) > (C_3{}^+ - C_3{}^+) > (C_1{}^+ - C_5{}^+)$, and the difference between former two groups is very small. The fact that the Ar^{8+} collisions and photoionization provide similar KER values is consistent with the nature of the excitation, which is considered to be electronic, and vibrational excitation would be solely resulting from the vertical transition.

To summarize the discussion, we can safely conclude that the D-loss will be a good criterion for the vibrational excitation, which gives an acceptable scheme for the dissociation. That is, when the vibrational energy of $(C_6D_6)^{2+}$ is not so large, the dissociation would be mainly governed by the potential surface, and thermodynamically favorable products, namely members of $(C_3{}^+ - C_3{}^+)$ group, are not necessarily to be formed preferentially. On the other hand, when vibrational energy is large, the shape of the potential surface does not play significant role, and thermodynamically favorable products are preferentially formed. Similar kind of coincidence measurements of larger aromatic hydrocarbons with the focus on fragmentation-mass shearing is will be performed in the near future.

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