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## Dissociative double photoionization of singly deuterated benzene molecules in the 26–33 eV energy range

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This work provides new experimental and theoretical results about the formation and dissociation of benzene dication. The experiment has been carried out by using a vacuum ultraviolet radiation from a synchrotron source together with a time-of-flight spectrometer and a position sensitive ion detector. Isotopically labeled benzene molecules with a single deuterium atom have been used in order to study the symmetric dissociation of the benzene dication, not well evident in previous experiments. A threshold of  $30.1 \pm 0.1$  eV has been observed for this dissociation reaction. Moreover, the lifetime of the dissociation of the benzene metastable dication producing  $\text{CH}_3^+$  and  $\text{C}_5\text{H}_3^+$  has been obtained as a function of the photon energy, by the use of a Monte Carlo trajectory analysis of the coincidence distributions. The determined lifetime is independent of the photon energy and has an average value of  $0.75 \pm 0.22$   $\mu\text{s}$ . Theoretical calculations of the energy and structure of dissociation product ions have been also performed to provide crucial information about the dynamics of the charge separation reactions following the photoionization event. © 2011 American Institute of Physics. [doi:10.1063/1.3646516]

### INTRODUCTION

The properties of molecular dications are rather different from those of both singly charged ions and neutral molecules. In solution, molecular dications are often stabilized by solvent interactions; however, in the gas phase they remain unstable in most cases. This is due to the strong Coulomb repulsion between the two charges that can induce the dissociation of the molecular dication into singly charged ions. However, in some cases the couplings by charge transfer effects can lead to the formation of metastable states.<sup>1–5</sup> It follows that the dynamics and the lifetimes of these doubly charged metastable states can selectively affect several microscopic and macroscopic phenomena. These doubly charged species play an important role in plasma chemistry and physics: a plasma may contain many molecular ions and, under some conditions, molecular dications can be present in not negligible concentrations. Molecular dications are also present in the ionosphere<sup>6</sup> of the earth or of other planets and are of interest in interstellar clouds and in hot material surrounding star forming regions.<sup>7</sup>

Theoretical calculations of the properties of molecular dications are far more difficult than similar calculations for neutral molecules or singly charged ions with equivalent numbers of electrons and nuclear masses. In fact, computing their

properties typically requires calculations which include extensively correlation effects using very large basis sets.<sup>2</sup>

The study of the dynamics of the dissociation reactions of these species, carried out at a molecular level, involves a detailed evaluation of the relative importance of fundamental components of intermolecular interactions, their strength, selectivity, and anisotropy, which can strongly affect the stability, the energy barriers in the dissociation channels, the dication lifetime and the kinetic energy release into ionic products. In particular, these observables depend not only on the Coulomb repulsion, that is the dominant interaction, but also on the critical balancing of other non-covalent contributions, such as size repulsion, induction, and dispersion attraction, and chemical contributions due to charge transfer effects. This aspect has been investigated in detail for relatively simple systems, such as hydrogen halide dications as, for instance,  $\text{HCl}^{2+}$ ,<sup>3,8</sup>  $\text{HBr}^{2+}$ ,<sup>5,9,10</sup>  $\text{HI}^{2+}$ .<sup>11</sup> In these systems, the metastability increases on going from HCl to HI because of the increasing importance of charge transfer coupling.<sup>4</sup> Very recently we have also experimentally investigated the dissociation of  $\text{N}_2\text{O}$ ,<sup>12,13</sup>  $\text{CO}_2$ ,<sup>14,15</sup> and benzene<sup>16</sup> dications, passing from simple diatomic to small polyatomic and aromatic molecules.

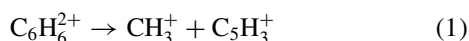
The simplest mechanisms by which gas phase molecular dications can be produced are electron impact ionization or double photo-ionization. Synchrotron radiation provides the possibility of studying the double-photo-ionization of molecules by a single photon absorption as high intensity

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light allows the observation of rather detailed features of the spectroscopy and dynamics of the parent ion and its fragments.

For the systems mentioned above the double ionization has been studied as a function of the photon energy, by measuring the ion products yield using time-of-flight (tof) mass spectrometry and, in the case of charge separation processes, by detecting the two fragment ions in coincidence. For HBr we have also measured in coincidence the two threshold photoelectrons,<sup>10</sup> obtaining interesting information about the low lying electronic and vibrational states of the molecular dication.

In a recent paper,<sup>16</sup> we have studied the benzene case, finding that the dication, once formed by double photoionization, that occurs with a threshold of 24.65 eV, is detected as doubly charged parent ion up to 27.8 eV, when the charge separation reaction



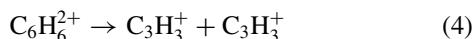
starts to occur. The second dissociative channel



opens at 29.5 eV, while a third process



starts at 30.2 eV. In earlier investigations,<sup>17,18</sup> the symmetric dissociation



has been also observed. However, in our recent experiment<sup>16</sup> we have been unable to clearly resolve this channel because the dication and the fragments appear at the same arrival time in the tof mass spectrometer. It has been only possible to guess the presence of this channel by the shape of the tof peak.<sup>16</sup> It has been observed that channel (1) also proceeds *via* the formation of a metastable state. The features of the coincidence data related to such a reaction can provide the lifetime of the metastable state by a statistical analysis. Three methods are mainly used in the analysis: one is based on a fit with some analytical functions,<sup>19</sup> another exploits a Monte Carlo simulation,<sup>19</sup> while a generalized simulated annealing statistical method has been very recently proposed by our laboratory.<sup>20</sup>

In order to achieve a more complete knowledge of the dynamics of the charge separation reactions of the benzene dication, in this work we present an investigation of the double photoionization by synchrotron radiation of mono-deuterated benzene molecules. This allows a better identification of the channel (4). In particular, the analysis of this new set of photoelectron-photoion-photoion coincidence data confirms the thresholds and energy dependence of the processes (1), (2), and (3) and provide crucial information on the isotopic variants of reaction (4). Moreover, we have analyzed the characteristics of the coincidence data related to reaction (1), with its isotopic variants, in order to obtain the lifetime of the benzene dication when dissociating *via* metastable states. In the previous paper,<sup>16</sup> we have also reported some theoretical calculations of the energetics and structure of involved molecular ions for the first three reactions. In the present study, we

have extended the calculations to also include channel (4). The combination of all experimental and theoretical data allows a deeper characterization of the dissociation dynamics of the benzene dication.

## EXPERIMENTAL

The typical experimental scheme that we exploited for measuring photoelectron-photoion-photoion coincidences is sketched in Fig. 1. The apparatus is operating at the synchrotron light laboratory ELETTRA (Trieste, Italy), in the ARPES end station of the Gasphase Beamline. Details about the beamline and the end station have been previously reported.<sup>12–16</sup> Only a brief description is given here. The energy selected synchrotron light beam crosses an effusive molecular beam of benzene molecules. This target gas is mixed with helium, employed for calibration reference measurements. The product ions are detected in coincidence with photoelectrons. The photon energy resolution provided by the monochromator is between 1.5 and 2.0 meV in the investigated energy range (26–33 eV). In order to avoid spurious effects due to the ionization by higher order diffraction photons, a magnesium film filter is placed along the synchrotron radiation beam path. The molecular benzene beam, the light direction, and the ion and electron detection axes are mutually perpendicular (see Fig. 1). The ion detection system has been assembled following the design described by Lavollée.<sup>21</sup> The details about how the electric field applies along the ion path are given and discussed in Ref. 20. Such a time-of-flight spectrometer, with an ion position sensitive detector, is

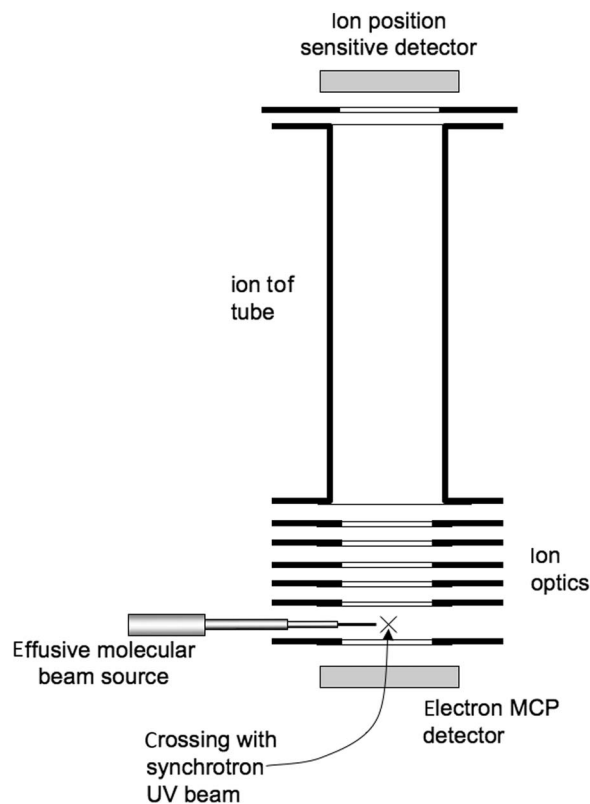


FIG. 1. Schematic representation of the experimental setup.

designed specifically to measure the spatial momentum components of the dissociation ion products.<sup>13,15</sup> In the present experiment, it has been used for determining the kinetic energy release in the ion products of the dissociative channels. The electron detector, located just below the interaction volume, consists of a stack of three micro-channel-plates followed by a copper anode. The ion detector also consists of a stack of three-micro-channel plates located at the end of a drift tube. The signals are read by an array of anodes arranged in 32 rows and 32 columns. Such an arrangement allows the detection of the ion arrival position on the detector plate. In our experiments, the photoelectron signals are used as start pulses, and then ions are counted as a function of their arrival time and position on the detector. All experiment components are controlled by a computer that also records experimental data.

As already mentioned above, the target gas is supplied to a needle beam source kept at room temperature, where it is also mixed with helium. This allows us to normalize all ion signals, at each photon energy, to the total ion yield of the rare gas signal measured at that energy. An adjustable leak valve along the gas inlet line is used to control the gas flow, which is monitored by recording the pressure in the main vacuum chamber. The incident photon flux and the gas pressure are monitored and stored in separate acquisition channels. Ion yields are then corrected for pressure and photon flux changes while varying the photon energy.

In order to better describe the matter reported above, we discuss the results of a real experiment. In Fig. 2 the plot of coincidences, as previously measured for the double photoionization of  $C_6H_6$  at 32.10 eV photon energy, is reported.<sup>16</sup> The formation of a stable  $C_6H_6^{2+}$  dication is quite evident (peak A), as well as the instantaneous dissociation into  $CH_3^+$  and  $C_5H_3^+$  (spot B), but also the same dissociation *via* a metastable dication (the tail from A to B). The channels (2) and (3) appear to be only instantaneous, that is without a tail (spots in the location C) in the time scale of our experiment.

From the size of the coincidence spots, we can define that the instrument recognizes as instantaneous dissociations those occurring in a time shorter than 50 ns, while the dications seen as stable are those living for a time longer than 2.2  $\mu s$ . Therefore, dissociations occurring *via* metastable dication states must happen in the time range between 50 ns and 2.2  $\mu s$ .

In order to extract also quantitative information, a numerical analysis of the distribution of coincidences is necessary. In early experiments<sup>19</sup> a procedure, based on approximated expressions, obtained from a kinematical analysis<sup>22</sup> has been exploited by Field and Eland.<sup>19,23</sup> In other cases, a Monte Carlo trajectory simulation of the ion flight inside the instrument has been used.<sup>19</sup> We have used both methods,<sup>14</sup> obtaining consistent results for the lifetime of the metastable dication and the kinetic energy release (KER) into the two product ions. Very recently we have also proposed a generalized

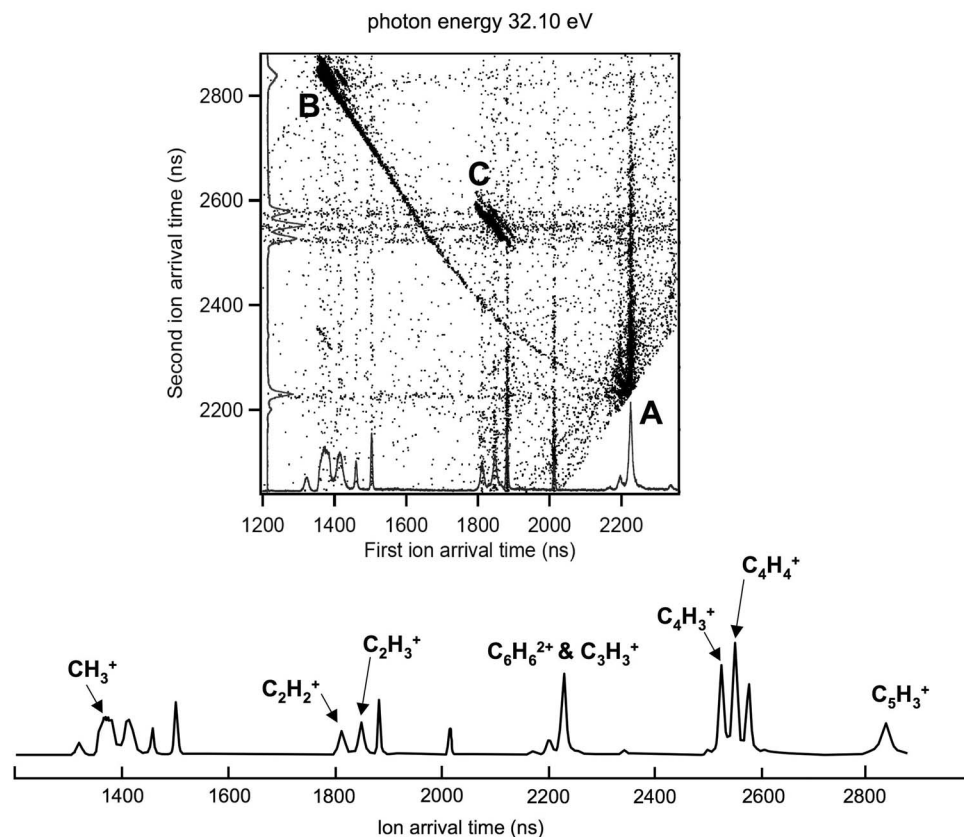


FIG. 2. Lower part: The time-of-flight mass spectrum of photoions detected with the photon energy set to 32.10 eV for non-deuterated benzene. Upper part: Ion-ion coincidence plot at the same energy. The points at the location A are a superposition of  $C_3H_3^+/C_3H_3^+$  coincidences and of the  $C_6H_6^{2+}$  dications. The points at the location B are the  $C_5H_3^+/CH_3^+$  coincidences, while those at C are  $C_2H_3^+/C_4H_3^+$  and  $C_2H_2^+/C_4H_4^+$  coincidences.

simulated annealing statistical method<sup>20</sup> that provides similar information.

## RESULTS AND DATA ANALYSIS

In Fig. 3 the coincidence plot analogous to that of Fig. 2 is reported, but for monodeuterated benzene at 32.0 eV photon energy. Similar plots have been obtained in the whole investigated photon energy range. The time scale of such plots is slightly different than that of the previous experiment because in the present setup the extraction and acceleration potentials have been modified in order to better optimize the mass resolution. The presence of a deuterium atom in the molecule produces the splitting of some of the mass spectrum peaks because the isotopic variants of product ions. This makes the analysis of the data more complicated, with respect to what it

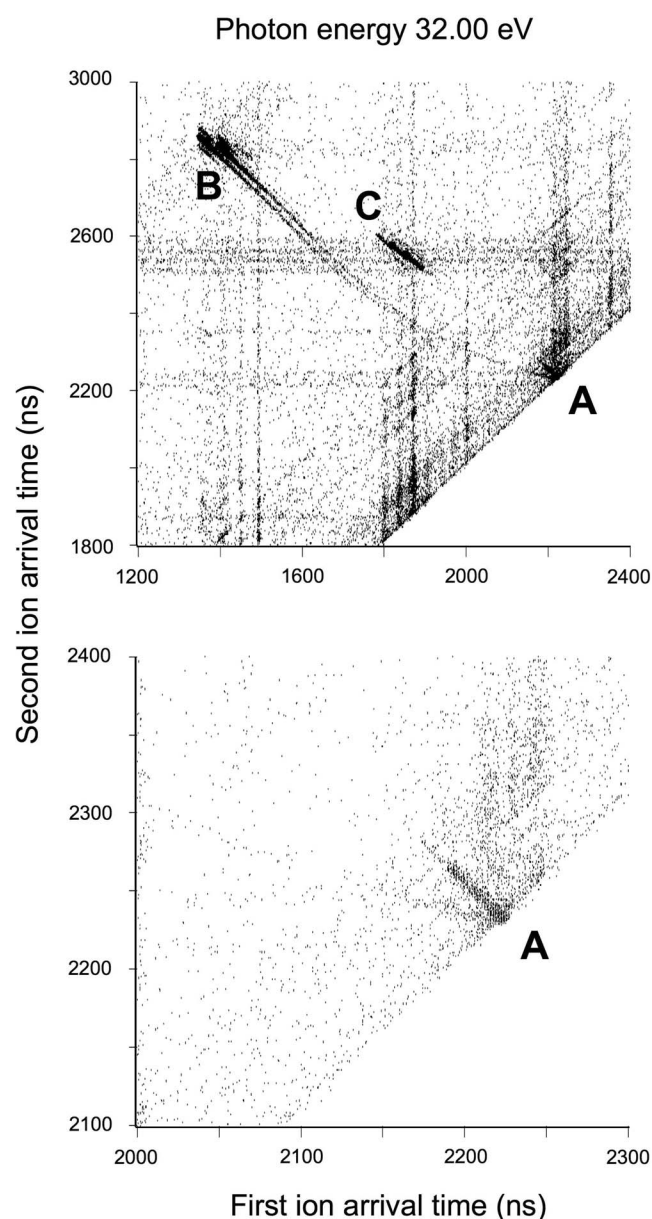


FIG. 3. Upper part: Time-of-flight spectrum as in the upper part of Fig. 2, for mono-deuterated benzene. Lower part: The coincidences around the location A are reported on an expanded scale.

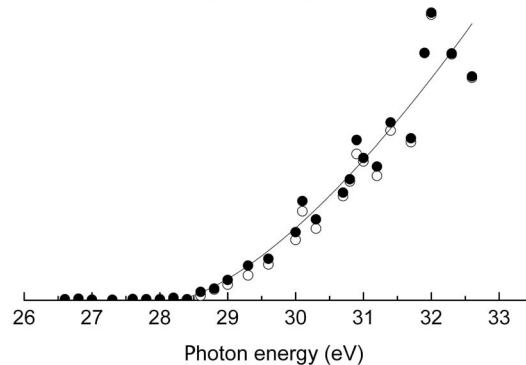
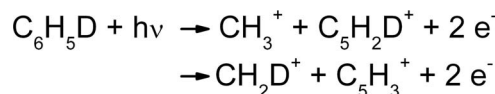


FIG. 4. Cross sections measured for the dissociation of the  $\text{C}_6\text{H}_5\text{D}^{2+}$  dication leading to  $\text{CH}_2\text{D}^+ + \text{C}_5\text{H}_3^+$  (open circles) and  $\text{CH}_3^+ + \text{C}_5\text{H}_2\text{D}^+$  (full circles). The two isotopic variants of products show a very similar behaviour. The line is the Wannier analysis used to obtain the threshold energy.

has been described in the previous work.<sup>16</sup> However, the reaction (4) is now quite evident (see location A in the lower panel of Fig. 3) and the analysis in terms of threshold and energy dependence becomes now possible. However, the spot of  $\text{C}_2\text{H}_3^+/\text{C}_2\text{H}_2\text{D}^+$  coincidences (the ribbon of points at almost  $45^\circ$  from A, in the lower panel of Fig. 3) is covering the region, where a possible tail for a metastable dissociation is expected and, therefore, is not possible to determine if this dissociation also occurs via a metastable state.

These data show consistency with results for  $\text{C}_6\text{H}_6$ . For the threshold energy of processes (1), (2), and (3), we obtain values that are consistent, within the experimental uncertainty ( $\pm 0.1$  eV), with those recently published for the non-deuterated benzene.<sup>16</sup> The thresholds have been extracted by the use of a Wannier function.<sup>24–26</sup> As an example, in Fig. 4 the cross sections measured for channel (1) are shown as a function of the photon energy. In this case, two sets of products are formed:  $\text{CH}_2\text{D}^+ + \text{C}_5\text{H}_3^+$  (open circles) and  $\text{CH}_3^+ + \text{C}_5\text{H}_2\text{D}^+$  (full circles). In the figure, it appears rather evident that the two isotopic variants show a very similar behavior, indicating a negligible isotopic effect for this dissociation reaction. However, looking closer to the data it could appear that the deuterated methyl ion is formed systematically with slightly lower intensity, suggesting a lower probability for such a channel. Nevertheless, the statistics of data do not allow a quantitative evaluation of such an effect.

In Fig. 5, the cross sections for process (4) are plotted as a function of the photon energy. The threshold is also in this case obtained by the use of a Wannier function<sup>24–26</sup> and a value of  $30.1 \pm 0.1$  eV has been found, which is very close to that of reaction (3). However, one has to point out that all the threshold energies for the four channels are smaller than those reported by Richardson *et al.*<sup>17</sup> more than 20 years ago as summarized in Table I, where the present results, those of our recent paper<sup>16</sup> and early ones,<sup>17</sup> are compared. Moreover, the KER for reaction (4), obtained here by a vector analysis, as it has been done in our previous work,<sup>16</sup> results to be  $3.8 \pm 0.1$  eV.

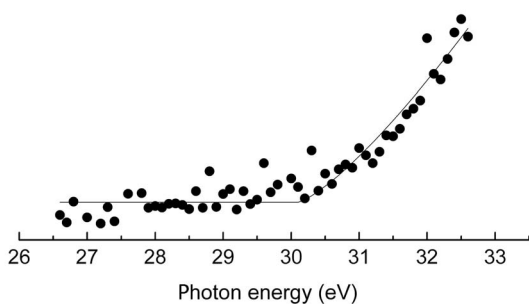
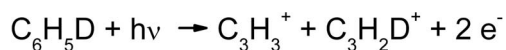


FIG. 5. Cross sections measured for the dissociation of the  $\text{C}_6\text{H}_5\text{D}^{2+}$  dication leading to  $\text{C}_3\text{H}_2\text{D}^+ + \text{C}_3\text{H}_3^+$ . The line is the Wannier threshold energy analysis.

To obtain the lifetime of the metastable dication states leading to the dissociation (1), it is necessary to analyze the distribution of coincidence points along the tails connecting the spots in the location B and the dication peak at the location A, both for the non-deuterated and the mono-deuterated benzene, as shown in Figs. 2 and 3. However, in the case of the singly deuterated benzene, the tail doubles, because the isotopic peaks separate in the vicinity of the spot B, merge in a single one in the vicinities of A. In order to avoid difficulties in the analysis because of such characteristics, once verified that the results are not appreciably affected by isotopic effects, we have analyzed the tail distribution as a function of the photon energy for the non-deuterated benzene only.<sup>16</sup> We have also verified, at a single photon energy, that the three analysis methods indicated above lead to identical results and, therefore, we have used the Monte Carlo procedure,<sup>19</sup> since the relevant routine resulted to be fast and has been well checked in our previous work.<sup>14</sup> In Fig. 6, the lifetimes as a function of the photon energy, obtained by the use of such an analysis, are reported. Within our experimental uncertainty no energy dependence is observed, the average value being  $0.75 \pm 0.22 \mu\text{s}$ .

## COMPUTATIONAL RESULTS

The potential energy surface of the system  $\text{C}_6\text{H}_6^{2+}$  and its fragmentation products was investigated by locat-

TABLE I. Dissociation reactions of the benzene dication.

Products <sup>a</sup>	Appearance energy (eV)		
	Ref. 6	Ref. 16	Present work
$\text{C}_5\text{H}_3^+ + \text{CH}_3^+$	$28.4 \pm 0.5$	$27.8 \pm 0.1^b$	$28.0 \pm 0.1$
$\text{C}_4\text{H}_3^+ + \text{C}_2\text{H}_3^+$	$31.3 \pm 0.5$	$29.5 \pm 0.1$	$29.6 \pm 0.1$
$\text{C}_4\text{H}_4^+ + \text{C}_2\text{H}_2^+$	...	$30.2 \pm 0.1$	$30.2 \pm 0.1$
$\text{C}_3\text{H}_3^+ + \text{C}_3\text{H}_3^+$	$32.2 \pm 0.5$	...	$30.1 \pm 0.1$

<sup>a</sup>In the case of the present work the mono-deuterated benzene has been used and; therefore, the products also contain a deuterium atom.

<sup>b</sup>This result is also in agreement with that of Ref. 18.

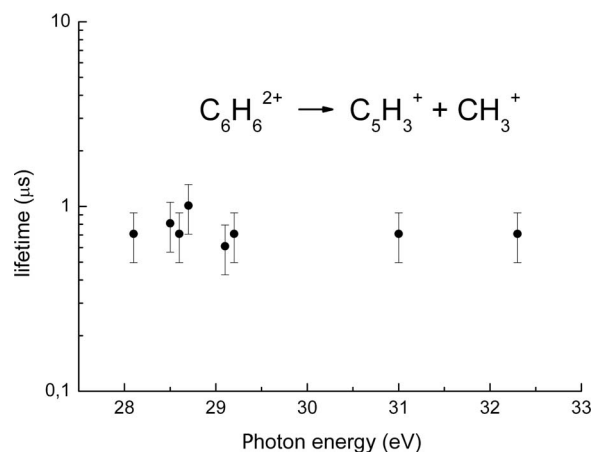


FIG. 6. The lifetime for the dissociation of the metastable state  $\text{C}_6\text{H}_6^{2+}$  dication as a function of the photon energy.

ing the lowest stationary points at the B3LYP (Ref. 27) level of theory in conjunction with the 6-311+G(*d*) basis set. At the same level of theory, we have computed the harmonic vibrational frequencies in order to check the nature of the stationary points, i.e., a minimum if all the frequencies are real, saddle point if there is one, and only one, imaginary frequency. The energy of all the stationary points was computed also at the higher level of calculation coupled-cluster singles and doubles plus perturbative triples (CCSD(T)) (Ref. 28) using the 6-311++G(3*df*,3*pd*) basis set. The B3LYP and the CCSD(T) energies were corrected to 298.15 K by adding the zero point energy correction and the thermal correction computed using the scaled harmonic vibrational frequencies evaluated at the B3LYP/6-311+G(*d*) level. All calculations were done using GAUSSIAN 03 (Ref. 29), while the analysis of the vibrational frequencies was performed using MOLEKEL.<sup>30</sup>

In order to study the dissociation reactions of  $\text{C}_6\text{H}_6^{2+}$  into  $\text{C}_5\text{H}_3^+ + \text{CH}_3^+$  and  $\text{C}_3\text{H}_3^+ + \text{C}_3\text{H}_3^+$ , we performed an optimization at B3LYP/6-311+G(*d*) level of the stationary points involved. The schematic reaction coordinate of these two dissociation reactions is shown in Fig. 7, where we have reported the relative enthalpies at 298.15 K computed at CCSD(T)/6-311++G(3*df*,3*pd*) level. TS<sub>3</sub> and TS<sub>4</sub>, which are true saddle points on the potential energy surface having only one imaginary frequency, lie slightly under the respective reactants when we include the zero point energy and the thermal corrections. The optimized structures, with the main geometrical parameters, of the minima and the saddle points are reported in Fig. 8.

For the sake of simplicity, in the following discussion we will consider only the more accurate CCSD(T) energies.

Reaction (4)  $\text{C}_6\text{H}_6^{2+} \rightarrow \text{C}_5\text{H}_3^+ + \text{CH}_3^+$  is strongly exothermic being the  $\Delta H_{298.15}^0$  computed to be  $-3.17 \text{ eV}$  at CCSD(T)/6-311++G(3*df*,3*pd*) level. This dissociation proceeds with the opening of the  $\text{C}_6\text{H}_6^{2+}$  ring which gives rise, through the saddle point TS<sub>1</sub>, to an open intermediate, which evolves to the products through the saddle point TS<sub>2</sub>. This mechanism is in agreement with the one previously reported by Anand and Schlegel.<sup>31</sup> The highest barrier is the second one which is 3.53 eV above  $\text{C}_6\text{H}_6^{2+}$ . Also reaction (1)

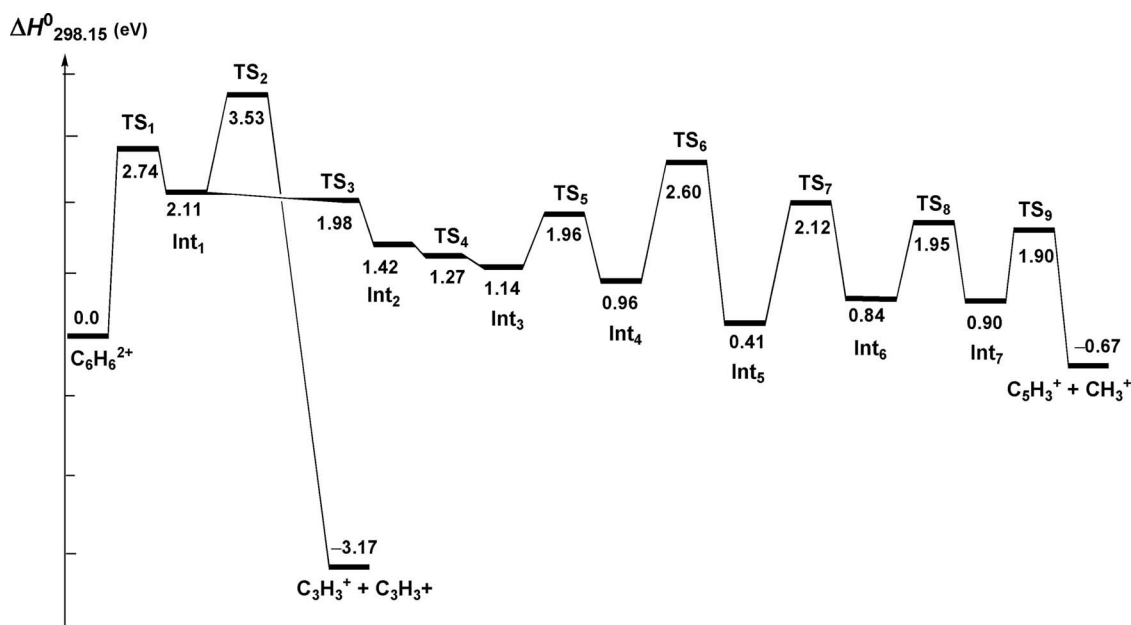


FIG. 7. Profile of the enthalpy changes at 298.15 K, computed at CCSD(T)/6-311++G(3df,3pd) level, for the two dissociation reactions  $\text{C}_6\text{H}_6^{2+} \rightarrow \text{C}_3\text{H}_3^+ + \text{C}_3\text{H}_3^+$  and  $\text{C}_6\text{H}_6^{2+} \rightarrow \text{C}_5\text{H}_3^+ + \text{CH}_3^+$ . For the labels of saddle points and minima, see Fig. 8.

$\text{C}_6\text{H}_6^{2+} \rightarrow \text{C}_5\text{H}_3^+ + \text{CH}_3^+$  is exothermic but its  $\Delta H_{298.15}^0$  is much smaller, in absolute value, being  $-0.668$  eV. However, this reaction shows a lower barrier than the first. Also this reaction starts with the opening of the  $\text{C}_6\text{H}_6^{2+}$  ring through

saddle points  $\text{TS}_1$ , but after this initial process the reaction mechanism involves several intermediates. However, the highest saddle point is the first,  $\text{TS}_1$ , which is 2.74 eV above  $\text{C}_6\text{H}_6^{2+}$ .

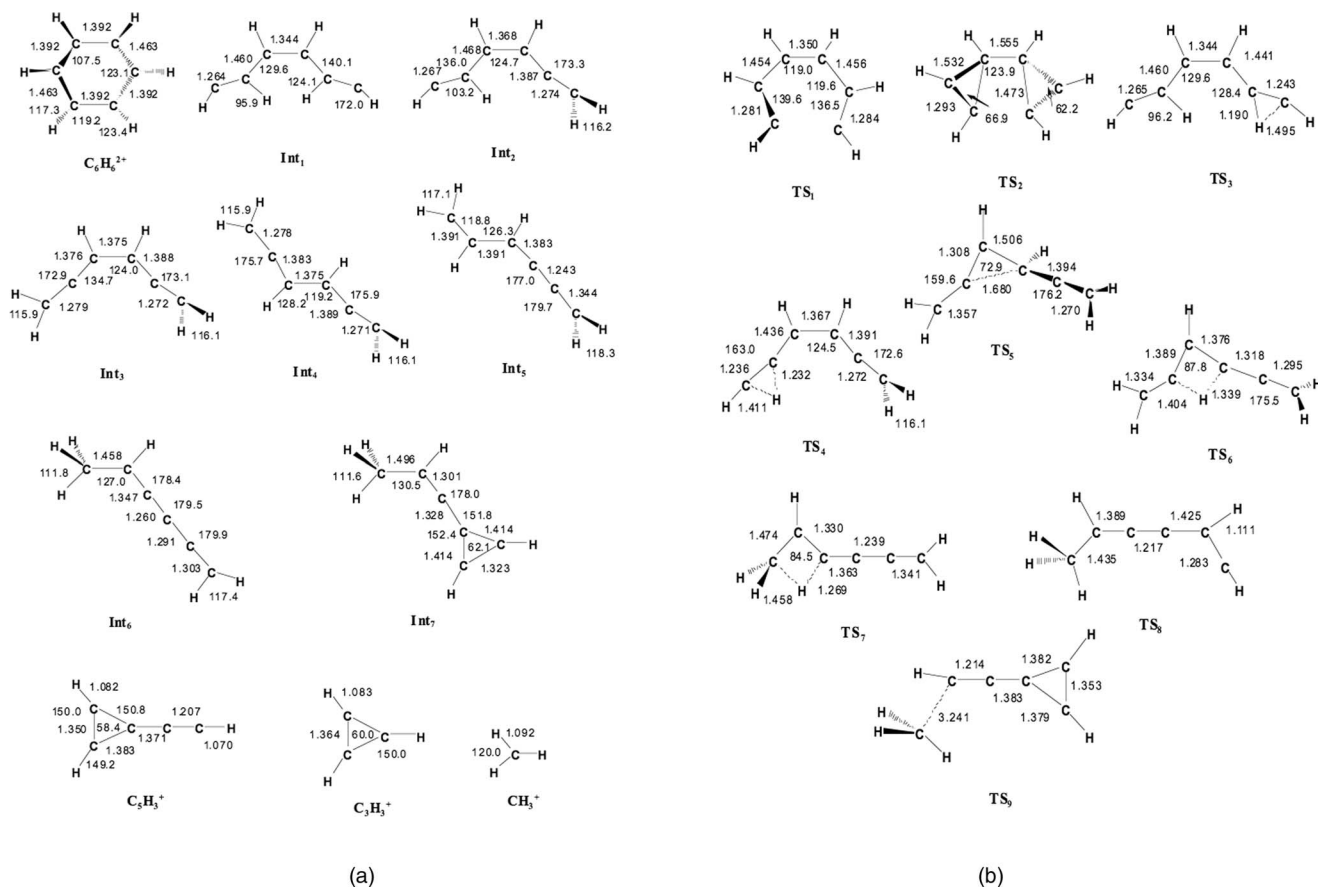


FIG. 8. B3LYP/6-311+G(d) optimized geometries (in Å and degrees) of the main stationary points investigated; (a) minima (b) saddle points.

## DISCUSSION AND CONCLUSIONS

It is possible to draw some important insights by joining the recent experimental results<sup>16</sup> about the double photoionization of C<sub>6</sub>H<sub>6</sub>, the present ones, about C<sub>6</sub>H<sub>5</sub>D, and the theoretical calculations here reported. It appears that the benzene molecule is doubly ionized and remains undissociated from 24.65 eV up to about 28 eV, on the time scale of our experiment. At photon energies higher than 28 eV, the dissociation (1) producing C<sub>5</sub>H<sub>3</sub><sup>+</sup>/CH<sub>3</sub><sup>+</sup> occurs, involving also a metastable channel. *Ab initio* calculations indicate that all dissociation channels in this range of energy involve an opening of the C<sub>6</sub>H<sub>6</sub><sup>2+</sup> ring. The metastability of reaction (1) could be attributed to the fact that, during the ring opening and rearrangement, two hydrogen nuclei must be transferred to form the final dissociation products. It is interesting to note that the present results appear consistent with the lower probability for the CH<sub>2</sub>D<sup>+</sup> formation channel, a slight trend also shown by our data. The lifetime of the metastable channel of this reaction has been found to be not affected by the photon energy. This observation suggests that this channel could be dominated by a vertical transition, leading to the dissociation of the dication.

At a photon energy of about 29.5 eV a dissociation leading to C<sub>4</sub>H<sub>3</sub><sup>+</sup>/C<sub>2</sub>H<sub>3</sub><sup>+</sup> also occurs, while at about 30.1 eV the two channels leading to C<sub>4</sub>H<sub>4</sub><sup>+</sup>/C<sub>2</sub>H<sub>2</sub><sup>+</sup> and C<sub>3</sub>H<sub>3</sub><sup>+</sup>/C<sub>3</sub>H<sub>3</sub><sup>+</sup> start to open. The first two processes are instantaneous, i.e., occurring in a time shorter than ~50 ns, while a contribution of metastable states to the third channel cannot be excluded based on our data.

It has to be noted that the experimental threshold energies cannot be compared with the features of the calculated minimum energy path: as it is well known, the experimental values are the average over energy distributions connected with the many possible dissociation paths. However, a comparison of the energy levels of final products, provided by *ab initio* calculations, with the experimental threshold energies and with the product ion KER values, strongly suggests that the dissociation ion products are formed with a high internal energy content, that can be structural, electronic, vibrational, and rotational. As an example, the reaction (4) exhibits an exothermicity of -3.17 eV, a threshold of 5.5 eV, and a KER of 3.8 eV, with respect to the molecular dication. This leads to an excess energy of 4.9 eV, which cannot be only vibrational and rotational.

As already noted above, the channels (1) and (2) require the movement of, respectively, two and one hydrogen nuclei. The channels (3) and (4) do not require instead any atom migration and they are simply promoted by the removal of two electrons from one of the two degenerate HOMOs of benzene.

It is interesting to note that when two electrons are removed from the HOMOs, if they are from each one of the two orbitals, a triplet state is formed, with an almost planar structure. On the other side, if the two electrons are spin coupled, they are removed from one of the two degenerate orbitals and a singlet state arises, with the formation of a distorted ring structure. In a recent paper,<sup>32</sup> Eland reports the spectrum of benzene dication produced by double photoionization. The

analysis of such a spectrum, when combined with some calculated energy levels,<sup>33</sup> appears to be consistent with the formation of the dication in a triplet ground state. However, other more recent theoretical works<sup>31,34</sup> found that the ground state is a singlet. In all calculations, the low lying triplet and singlet states appear to be very close in energy.<sup>31,33,34</sup> The present theoretical results confirm that the most stable state is a singlet one. It has also to be noted, when looking at the spin of product ions, that the dissociative channels here studied are consistent with a precursor dication in a singlet state. Obviously, the triplet and singlet states can be formed in the investigated photon energy range, but only the singlet is involved in the dissociation channels.

We believe that all this information is important for a better understanding of the phenomena where double photoionization and fragmentation of benzene are involved.

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<sup>1</sup>L. Pauling, *J. Chem. Phys.* **1**, 56 (1933).

<sup>2</sup>S. G. Cox, A. D. J. Critchley, P. S. Kreynin, I. R. McNab, R. C. Shiellx, and F. E. Smith, *Phys. Chem. Chem. Phys.* **5**, 663 (2003).

<sup>3</sup>M. Moix-Teixidor, F. Pirani, P. Candori, S. Falcinelli, and F. Vecchiocattivi, *Chem. Phys. Lett.* **379**, 139 (2003).

<sup>4</sup>P. Candori, S. Falcinelli, F. Pirani, F. Tarantelli, and F. Vecchiocattivi, *Chem. Phys. Lett.* **436**, 322 (2007).

<sup>5</sup>M. Alagia, B. G. Brunetti, P. Candori, S. Falcinelli, M. Moix-Teixidor, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **120**, 6985 (2004).

<sup>6</sup>S. S. Prasad and D. R. Furman, *J. Geophys. Res.* **80**, 1360 (1975).

<sup>7</sup>S. D. Rosner, R. Cameron, T. J. Scholl, and R. A. Holt, *J. Mol. Spectrosc.* **189**, 83 (1998).

<sup>8</sup>M. Alagia, F. Biondini, B. G. Brunetti, P. Candori, S. Falcinelli, M. Moix-Teixidor, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **121**, 10508 (2004).

<sup>9</sup>M. Alagia, M. Boustimi, B. G. Brunetti, P. Candori, S. Falcinelli, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **117**, 1098 (2002).

<sup>10</sup>M. Alagia, B. G. Brunetti, P. Candori, S. Falcinelli, M. Moix-Teixidor, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **120**, 6980 (2004).

<sup>11</sup>M. Alagia, B. G. Brunetti, P. Candori, S. Falcinelli, M. Moix-Teixidor, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **124**, 204318 (2006).

<sup>12</sup>M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *Chem. Phys. Lett.* **432**, 398 (2006), and references therein.

<sup>13</sup>M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Chem. Phys.* **126**, 201101 (2007).

<sup>14</sup>M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Phys. Chem. A* **113**, 14755 (2009).



- <sup>15</sup>M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *Phys. Chem. Chem. Phys.* **12**, 5389 (2010).
- <sup>16</sup>M. Alagia, P. Candori, S. Falcinelli, F. Pirani, M. S. Pedrosa Mundim, R. Richter, M. Rosi, S. Stranges, and F. Vecchiocattivi, *Phys. Chem. Chem. Phys.* **13**, 8245 (2011).
- <sup>17</sup>P. J. Richardson, J. H. D. Eland, and P. Lablanquie, *Org. Mass Spectrom.* **21**, 289 (1986).
- <sup>18</sup>D. M. P. Holland, D. A. Shaw, I. Sumner, M. A. Bowler, R. A. Mackie, L. G. Shpinkova, L. Cooper, E. E. Rennie, J. E. Parker, and C. A. F. Johnson, *Int. J. Mass Spectrom.* **220**, 31 (2002).
- <sup>19</sup>T. A. Field and J. H. D. Eland, *Chem. Phys. Lett.* **211**, 436 (1993).
- <sup>20</sup>M. Alagia, P. Candori, S. Falcinelli, K. C. Mundim, M. S. P. Mundim, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, "Lifetime and kinetic energy release of metastable dications dissociation," *Chem. Phys.* (in press).
- <sup>21</sup>M. Lavollée, *Rev. Sci. Instrum.* **70**, 2968 (1999).
- <sup>22</sup>S. Hsieh and J. H. D. Eland, *J. Phys. B* **30**, 4515 (1997).
- <sup>23</sup>A. E. Slattery, T. A. Field, M. Ahmad, R. I. Hall, J. Lambourne, F. Penent, P. Lablanquie, and J. H. D. Eland, *J. Chem. Phys.* **122**, 084317 (2005).
- <sup>24</sup>G. H. Wannier, *Phys. Rev.* **90**, 817 (1953).
- <sup>25</sup>B. Eckhardt and K. Sacha, *Europhys. Lett.* **56**, 651 (2001).
- <sup>26</sup>S. Denifl, P. Candori, S. Ptasinska, P. Limão-Vieira, V. Grill, T. D. Märk, and P. Scheier, *Eur. Phys. J. D* **35**, 391 (2005).
- <sup>27</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- <sup>28</sup>R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981); K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989); J. Olsen, P. Jorgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).
- <sup>29</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision D.01, Gaussian, Inc., Wallingford, CT (2004).
- <sup>30</sup>P. Flükiger, H. P. Lüthi, S. Portmann, and J. Weber, MOLEKEL 4.3, Swiss Center for Scientific Computing, Manno (Switzerland), 2000–2002; S. Portmann and H. P. Lüthi, *Chimia* **54**, 766 (2000).
- <sup>31</sup>S. Anand and H. B. Schlegel, *J. Phys. Chem. A* **109**, 11551 (2005).
- <sup>32</sup>J. H. D. Eland, *Chem. Phys.* **345**, 82 (2008).
- <sup>33</sup>F. Tarantelli, A. Sgamellotti, L. S. Cederbaum, and J. Schirmer, *J. Chem. Phys.* **86**, 2201 (1987).
- <sup>34</sup>M. Rosi, C. W. Bauschlicher, Jr., and E. L. O. Bakes, *Astrophys. J.* **609**, 1192 (2004).