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Strong isotopic selectivity on dication formation of benzene

L. Sigaud[*]
Universidade Federal Fluminense, Niterói 24210-346, Brazil

W. Wolff[†] and E. C. Montenegro[‡]
Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-972, Brazil

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Double ionization of benzene initiates a competition between its fragmentation driven by Coulomb repulsion and dication stabilization, in which the molecule undergoes a strong geometric rearrangement. We find experimentally that stabilization following an electron-impact-induced double-ionization is remarkably sensitive to the isotopic replacement of just one ^{13}C atom in the benzene ring. This result has no analog in dications of smaller molecules. The large reactivity of medium-size hydrocarbon dications points towards an alternative route to imprint isotopic signatures in astrophysical processes.

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I. INTRODUCTION

The removal of two electrons in intermediate-sized molecules causes an enormous disturbance in molecular bonding, such that, in most cases, the bonds are not sustained and the molecule breaks up. There is, however, the possibility of a reorganization of the chemical bonds forming a metastable dication. This stabilization can be accompanied by a significant change in molecular geometry, and such is the case of benzene. Although calculations of the initial and final states of the molecule are available in the literature [1–4], a detailed description of the process in its transient phase has not been done so far, even for smaller and simpler molecules. This is due to its complexity since it depends on the orbitals from which electrons are removed, the electron correlation of the remaining electrons, and the various possible paths for nuclear rearrangement to form a final stable molecular state.

Some light on the transient phase of this conformational change can be gained with a marker that can increase or decrease the probability of obtaining a dication. Isotopic substitutions were used for this purpose, in particular with deuterated species [5–7]. Therefore, differences in nuclear masses can augment or hinder the fragmentation of doubly ionized species. However, to identify the level of sensitivity that a breaking in the symmetry of the mass distribution has in the stabilization of the system, the substitution of a single ring atom of ^{12}C by a ^{13}C isotope would constitute a much fainter marker.

Going against this reasoning, it is widely assumed that molecular fragmentation is independent of isotopic differences in its main structural components, i.e., for nuclei heavier than hydrogen. This paradigm has not been questioned so far. Indeed, this feature has been employed by many authors to obtain molecular dication production cross sections in those cases where the parent molecule has an even symmetry with respect to its constitutional elements (e.g., N_2, O_2, benzene, etc.) by using a heteroisotopic analog to identify the dication contribution [1,8–13]. The measurement of the dication production of such molecules cannot be performed directly in a standard time-of-flight (TOF) spectrometer since it does not separate moieties with the same mass-to-charge ratio. In this work, we show that this procedure is not always reliable and that the replacement of a single ^{13}C atom in the benzene ring is capable of changing the yield for dication production substantially.

Nevertheless, polycyclic aromatic hydrocarbons (PAH's) in the gas phase are present in a wide spectrum of environments from the interstellar medium (ISM) and planetary atmospheres [14,15] to soot in combustion engines [13], with benzene being the seed structure for building larger PAH's. When energized, stable PAH's dications are produced, playing an important role in the evolution, in the identification of the composition of these environments, and in the scrutiny of their energization levels. In this wide area of investigation, the knowledge of production paths, stability, and emission spectra of PAH's dications are essential and an object of theoretical and experimental investigation, e.g., as an input for the feeding of fast postcollision ionic chemistry simulations, by providing specific signatures in the IR emission from the interstellar medium, or as markers in the identification of soot inventories in combustion chambers [13–16]. A second question that arises is whether this isotopic substitution would alter not only the dication's stability during its formation process, but also its lifetime. This issue is also addressed in this work.

It must be noted that it is much more likely to find natural isotopic substitutions, as far as hydrocarbons are concerned, of carbon than of hydrogen atoms since the $^{13}C / ^{12}C$ isotopic ratio on Earth (1.1%) is ~100 times larger than for $^{2}H / ^{1}H$ [17]. This proportion holds in the vicinity of stars, including the solar system [18,19], albeit not for the interstellar medium, where the $^{2}H / ^{1}H$ ratio can be much larger [20]. As a

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[*] lsigaud@id.uff.br
[†] wania@if.ufrj.br
[‡] montenegro@if.ufrj.br

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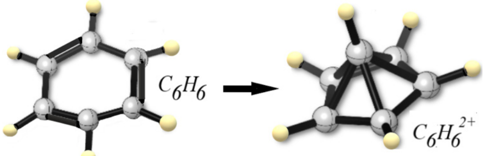

FIG. 1. Diagram illustrating the geometrical rearrangement of the carbon atoms of benzene after the removal of two electrons [2–4]

consequence, ionization mechanisms that present a selectivity on their final products can imprint different isotopic signatures depending on the molecule's environment.

Atmospheric physical chemistry, accessed by ionizing radiation, is directly influenced by the presence of dications since they are a extremely reactive species [21–24]. Besides that, due to their metastable nature leading to the production of two charged fragments, the resulting Coulombic repulsion provides kinetic energy releases of the order of tens of electron volts, introducing more energetic contributions to subsequent secondary reactions [25–27]. Moreover, the absorption of energy involved in dication formation and its release in secondary reactions contribute to ionospheric energizing, leading to temperature increases and planetary escape [28–31].

Disentangling and identifying two different moieties with the same mass-to-charge ratio is possible with the delayed extraction time-of-flight (DETOF) technique [32]. Benzene falls into the same category as N_2, O_2, and C_2H_4 as far as the measurement of its dication goes. However, at variance with these simpler molecules' dications which retain the same geometrical conformation than their respective neutral parent molecule, $C_6H_6{}^{+2}$ undergoes a strong rearrangement of its geometrical structure between its initial and final states [2–4]. This process is illustrated in Fig. 1, where we show the original molecule in its planar configuration and the doubly ionized species, no longer an aromatic ring, with one of the carbons leaving the original geometrical plane and assuming a pyramidal configuration. It is shown here that this change in the geometry leads to significant differences between $C_6H_6{}^{+2}$ and $^{13}CC_5H_6{}^{+2}$ production rates. Indeed, and contrary to common assumptions, it is somehow surprising that the stability of the final state of the dication depends on such a small difference in the mass of one of the constituents of the carbon ring since its influence in the molecular orbitals is negligible.

II. EXPERIMENTAL SETUP

The experimental apparatus, a TOF spectrometer, was described in detail before [33]; in short, it consists of an electron gun operating in the 30–800 eV energy range and a TOF spectrometer coupled to a gas cell. A synchronism between the electron beam pulse and the extraction field pulse form the basis of the already well-established DETOF technique [32], which consists on varying the time delay between an electron beam and an ion-collector pulses, and recording the recoil ions still present in the collection region afterwards. By taking TOF spectra for a wide range of time delays and measuring the collected ions for a particular m/q ratio peak, a profiling of the kinetic energy distributions can be determined [32]. For this work, spectra for 26 different values of time delay for each presented impact energy were measured. Therefore, the relative weight given to each kinetic energy distribution present in the analyzed peak corresponds to its fraction produced via the mechanism(s) leading to that kinetic energy distribution.

The benzene sample is a high-purity one in liquid state at room temperature, and was prepared by performing many freeze-pump-thaw cycles before being admitted to the pressure and flow controlled gas line that feeds the gas cell. A constant gas flow was further ensured by keeping the benzene samples cooled down to ~260 K during measurements [1].

Two species that compose a single peak in the TOF spectra, namely the doubly ionized benzene molecule ($C_6H_6{}^{+2}$), which acquires no kinetic energy in the collision process and retains the same original Maxwell-Boltzmann distribution as the parent ion, and the singly charged fragment with the same mass-to-charge ratio ($C_3H_3^+$), which gains kinetic energy via momentum conservation in the fragmentation process, can be disentangled [34,35]. Thus, by quantifying the relative weights of the kinetic energy distributions, the yields of each moiety can be directly obtained. This also means that the yields for both dicationic species, the never directly measured $C_6H_6{}^{+2}$ and its isotopic variant $^{13}CC_5H_6{}^{+2}$, can be obtained (and compared) in a single experiment. On the other hand, it was observed that the $C_3H_3^+$ fragment is produced by a combination of an exponential kinetic energy distribution (corresponding to ions with suprathermal kinetic energy, coming from fragmentation with resulting low velocities of its products) and two Gaussian kinetic energy distributions (representing more violent fragmentation processes). The spectrometer's efficiency was established by measuring argon, krypton, ethylene, molecular oxygen, and molecular hydrogen, and comparing them with the literature, following the procedure described in Ref. [33]. The criteria for the analysis are that the adjustment to the different kinetic energy distributions to the raw data of each peak has to have an adjustment parameter R^2 above 0.99 and that the error bars are adopted by keeping R^2 above 0.97 [35].

Mass spectra for 70 eV electron impact energy for the minimum delay time and for an 8-μs delay time are shown, normalized by the parent ion, and superposed for comparison, in Fig. 2. The resolution of the apparatus and the effect that the free flight-time employed with the DETOF technique has on the fragment peaks can be seen. In Fig. 2 a zoomed-in view of the TOF region comprising the two dicationic species is also shown to depict the two neighboring peaks, $^{13}CC_5H_6^{2+}$ and $C_6H_6^{2+}$, clearly separated. Since the $^2H\,/\,^1H$ ratio is ~1% of the $^{13}C\,/\,^{12}C$ one, the contribution of the other possible isotopically substituted benzene, $^{12}C_6{}^2H^1H_5^{+2}$, can be considered negligible.

III. RESULTS AND DISCUSSION

Figure 3 shows the results for both $^{13}CC_5H_6{}^{+2}$ and the parent ion $C_6H_6^+$ with respect to the different measured delay times. The data are presented as the ratio between the measured species for a delay time t and its value for the minimum delay time t_0 and it is compared to the ones reproduced from the Maxwell-Boltzmann kinetic energy distribution, with perfect agreement within the experimental uncertainties [32,34,35]. This means that the Maxwell-Boltzmann

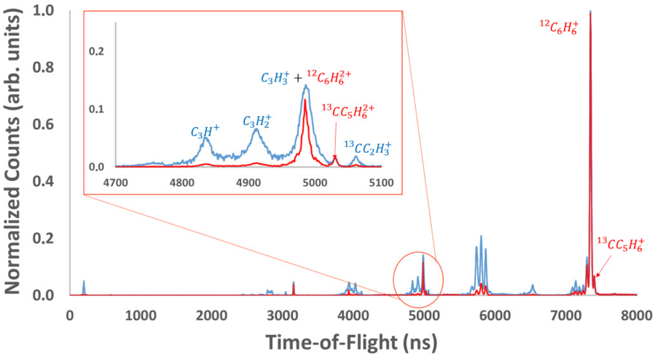

FIG. 2. Mass spectra for sample two out of 26 time delays measurements performed: our minimum delay time, upper (blue or light gray) line, and 8-μs delay time, lower (red or dark gray) line, at 70-eV electron impact energy. The differences between the amount of ions present are easily discernible, in particular how most fragmented moieties have left the collection region while most unfragmented species have not. A zoom of the main studied group's TOF region, comprising the two dicationic species and fragments with similar m/q ratio, is shown in the inset.

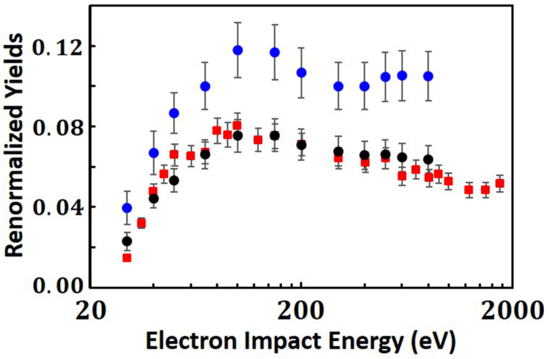

FIG. 4. Ratio between benzene dication and parent ion with respect to the electron impact energy (eV). Present work, $C_6H_6{}^{+2}$, and $^{13}CC_5H_6{}^{+2}$, blue (gray) and black circles, respectively; Wolff *et al.* [1] $^{13}CC_5H_6{}^{+2}$ renormalized by the present yields at 200-eV impact energy, red squares. The error bars of the present work are estimated by the composition of statistical and normalization uncertainties with the ones coming from the DETOF analysis, which is detailed elsewhere [35].

distribution is calculated considering that the measured recoil ion does not decay, i.e., both species have a lifetime long enough that our experiment cannot infer an absolute value. Nevertheless, by modulating the Maxwell-Boltzmann distribution curve by an exponential decay function ($e^{-t/\tau}$, where τ would be the ion's lifetime) and taking into account the experimental uncertainties of the reported data, one can establish a lower boundary for the metastable dication lifetime. Looking at the different lifetimes indicated in Fig. 3, we can place the minimum value of $^{13}C\,C_5H_6{}^{+2}$ at ~200 μs.

The same behavior was also observed for $C_6H_6{}^{+2}$, with the same lower limit for its lifetime; its data are not shown here due to its convolution with the higher kinetic energy distributions of the $C_3H_3^+$ fragment, but the shape of the analyzed data for higher delay times, where the contribution coming from the fragmented, faster species to the total is already negligible, is equivalent to its heteroisotopic counterpart. Hence, dicationic metastable decay plays no role on the present measurements and provides no perceptible difference between homo- and heteroisotopic benzene dications. It must be noted that doubly ionized species that undergo fragmentation with lifetimes below the total flight time of 4.5 μs inside the setup's TOF are not measured here.

Previous data on the literature of benzene dication produced by electron impact focus solely on the heteroisotopic species [1,11,12], and only the data from Wolff *et al.* [1] were performed over a wide impact energy range, while Hustrulid *et al.* [11] and Engel *et al.* [12] reported data only for 70-eV impact energy. It must be noted that the present measurements are independent of the spectrometer's absolute or relative efficiencies, since $C_6H_6{}^{+2}$ and $^{13}CC_5H_6{}^{+2}$ have the same charge state and only a 0.5 difference in its mass-to-charge ratio, which is negligible for efficiency purposes. Since both species were directly measured in the same experiment, differences in their relative behavior cannot come from the setup's efficiency and/or uncertainties, and therefore must reflect particular properties in their production.

In Fig. 4 our results are presented alongside the $^{13}CC_5H_6{}^{+2}$ data of Wolff *et al.* [1] renormalized by the present yields at 200-eV impact energy for comparison. It can be seen that there is a marked difference between the ratio for $C_6H_6{}^{+2}$ and $^{13}CC_5H_6{}^{+2}$ with respect to the parent ion. The isotopic ratio of the parent ion follows the natural abundance: (6.49 ± 0.31)% compared to the expected 6.6% for the combined six carbon atoms present in benzene; for the stable dications, on the other hand, this isotopic ratio falls to (4.21 ± 0.45)%. This feature is independent of the spectrometer's efficiency when determined at the same measurement. This means that there is, indeed, a strong selectivity on the production of the metastable

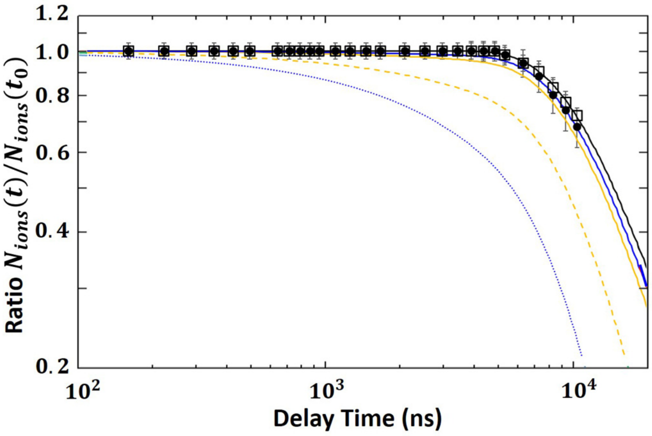

FIG. 3. Ratio between product ions for a delay time t and the minimum delay time t_0 for $^{13}CC_5H_6{}^{+2}$ (closed circles) and the parent ion $C_6H_6^+$ (open squares), in comparison with the Maxwell-Boltzmann kinetic energy distribution (full black line). Maxwell-Boltzmann curves modulated by $e^{-t/\tau}$ decay functions are also presented for τ values of 10 μs [dotted blue (dark gray) line], 23 μs [dashed orange (light gray) line], 100 μs [full orange (light gray) line], and 200 μs [full blue (dark gray) line].

doubly charged benzene regarding isotopic changes in one of its carbon atoms.

The behavior of both $C_6H_6{}^{+2}$ and ${}^{13}CC_5H_6{}^{+2}$ normalized by the parent ion, with respect to the increase of the electron impact energy, shows that, after an increase after the ionization potential is crossed, there is a peak on the yields around 70 eV followed by a soft descent and further stabilization at almost constant values. It can be seen in Fig. 4 that the ${}^{13}CC_5H_6{}^{+2}$ yields for both datasets follow the same behavior, showing that there is no detectable differences observed for the mechanisms for ${}^{13}CC_5H_6{}^{+2}$ production. The data of Wolff *et al.* [1] are also not affected by the dication's lifetime since their setup has an estimated flight time of 23 μs (which corresponds to the lifetime depicted by the dashed orange curve of Fig. 3).

The peaked structure followed by a nearly constant asymptotic behavior with respect to the impact energy is characteristic of a competition between two double ionization mechanisms: TS-2 double vacancy production, which presents a $\sim 1/E$ on the dication-parent-ion ratio with respect to the impact energy, and single carbon K-shell ionization followed by Auger decay, which presents a constant tendency due to the fact that both dication and parent ion come from single vacancy production processes [34]. This combination of direct double ionization and single ionization followed by postcollisional autoionization is similar to what was observed for ethylene dication formation as well [35]. Figure 4 also shows that the two processes are present for both $C_6H_6{}^{+2}$ and ${}^{13}CC_5H_6{}^{+2}$ production, with no significant contrast in the shape of the dataset. This indicates that the difference on the yields do not come from an isotopic effect on the mechanisms of metastable dication production.

This leads to the conclusion that the marked differences on the $C_6H_6{}^{+2}$ and ${}^{13}CC_5H_6{}^{+2}$ yields are independent of its production mechanism. Direct double vacancy production happens during the collision process, whose time frame is in the attosecond range, whereas the Auger decay following ionization of an inner shell occurs in the femtosecond scale [35]. This result is a signature of an ultrafast migration of electrons driven by electronic correlation [36]. In fact, in the direct double vacancy production mechanism electrons are more likely to be removed from different sites on the benzene ring. In Auger decay, on the contrary, both electrons are removed from a single carbon atom. This process would not contribute so efficiently to the formation of the dication unless an ultrafast charge migration towards the same charge distribution resulting from double collision occurs before the rupture of the ring.

Thus, the origin of such difference on the dications production must come from a process slower than the electronic orbitals reconfiguration. This leads to the conclusion that the transition from a planar carbon ring to a pyramidal configuration must be the cause for the different yields of $C_6H_6{}^{+2}$ to ${}^{13}CC_5H_6{}^{+2}$, which are independent of the measuring conditions. The substitution of a single carbon atom ${}^{12}C$ for its stable isotope ${}^{13}C$, which increases by a unit the mass of one of the components of the carbon ring and has essentially no effect on the electronic molecular orbitals, provokes a more unstable rearrangement process after two electrons are removed, and the benzene nuclei are taken to a new geometry, with one of its carbons leaving the original molecular plane, as illustrated in Fig. 1. In the transient phase of benzene conformational change, shrinkage of the ring occurs where one of the C atoms is moved to the top of the pyramid. Assuming that the blow up of the molecule is enhanced if this shrinkage occurs where ${}^{13}C$ or one of its first close neighbors are located, the statistical reduction in the stabilization of dications would be ~50% since it comprises three out of the six possible shrinkage sites of the doubly ionized molecule. This conjecture agrees with the observed ~40% reduction of the yield of the dication production from $C_6H_6{}^{+2}$ to ${}^{13}CC_5H_6{}^{+2}$.

IV. CONCLUSION

Dications of the same molecule, but with different isotopic species, can be produced with different yields, if subsequent geometrical rearrangements after ionization takes place. Our findings show that “pure” ${}^{12}C_6H_6$ dication is more likely to be produced when compared with the heavier isotope ${}^{13}C\,{}^{12}C_5H_6{}^{+2}$. As a consequence, the fact that a single isotopic substitution in the aromatic ring leads to such drastic differences shows that the commonly used procedure of inferring molecular dication yields of symmetric homoisotopic molecules from heteroisotopic analogs can lead to unreliable results. Thus, the results presented here establish a paradigm shift on the determination of dicationic production involving conformational geometrical changes, where a single mass asymmetry in the molecular ring composition can favor fragmentation. For example, naphthalene ($C_{10}H_8$) changes its geometry from two adjacent rings arranged on a plane to one open elliptically shaped ring in its dicationic form [37].

Moreover, the description of the transient phase between the removal of two electrons and the final metastable dicationic state, including the electronic orbitals' reconfiguration and the consequent nuclear geometrical rearrangement, must rely on theoretical models or computational simulations that take these isotopic differences into account and consists of a very stringent test of such models.

Furthermore, due to the high reactivity of long-lived doubly charged species [22], environmental effects which are related to the presence of dications may have some isotopic selectivity imprinted. Benzene is known, for example, to be present on the planetary atmospheres of Earth, Jupiter, and Saturn [38–40], as well as in Titan's ionosphere [41]. In particular, it is a building block in the chemistry of interstellar media [14] as a major contributor to the formation and growth of larger clusters of polycyclic aromatic hydrocarbons in the ISM [15], where it can be irradiated by high-energy cosmic rays or ultraviolet photons [16]. The isotopic abundances of carbon atoms in ISM molecules are still an open issue [42], and our findings show that isotopic selectivity of the stable products of ionization processes cannot be ruled out.

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