How a single replacement of 13C in a benzene ring strongly affects dication formation induced by swift projectiles

L Sigaud[1] *, W. Wolff[2] and E C Montenegro[2]

[1]Instituto de Física, Universidade Federal Fluminense, Niterói, 24210-346, Brazil
[2] Instituto de Física, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 21941-909, Brazil

Synopsis Double ionization of molecules trigger a competition process between fragmentation and stabilization in a molecular dication. We find experimentally that stabilization of benzene 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 double ionization of benzene initiates a competition between its fragmentation, driven by Coulombic repulsion, and its stabilization as a molecular dication. Nevertheless, from the fundamental neutral state to the metastable state with two fewer electrons the molecule undergoes a strong geometrical rearrangement of its constituents, with one of the carbon nuclei leaving the original geometrical plane, as shown in Figure 1.

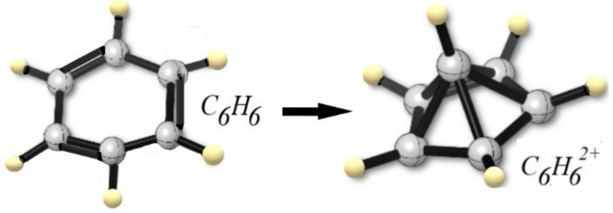

Figure 1. Pictorical representation of the change in the molecular geometry of benzene as it becomes a dication.

The mass spectrometry detection of the benzene dication is hindered by the difficulty of disentangling it from the molecular fragment $C_3H_3^+$, since both have the same mass-to-charge ratio (*m/q*). Usually, in molecules with an even symmetry (e.g. N_2 and O_2 [1]), this problem is circumvented by means of an isotopic analogue of the molecular dication, providing a *m/q* different than the one for the molecule broken in half – in this case, $^{13}C^{12}C_5H_6$ [2]. With the DETOF technique, the dication production for this class of molecules can be measured directly [3].

In this work, the double ionization of the benzene molecule was studied for electron impact ranging from 30 to 800 eV. Via the DETOF technique, the different kinetic energy distributions present for each peak of the time-of-flight spectra were determined. Thus, the molecular dication of benzene, which retains the same Maxwell-Boltzmann distribution as the parent molecule, can be distinguished from the $C_3H_3^+$ fragment, which acquires kinetic energy in the breakup process. The dication production for the molecule with an isotopic substitution of ^{13}C in the aromatic ring was also obtained.

The experimental results [4] show that the stabilization after double ionization of the benzene molecule is extremely sensitive to this single carbon isotopic substitution. A difference of approximately 40% more production of $^{12}C_6H_6^{2+}$ than that of $^{13}C^{12}C_5H_6^{2+}$ was observed [4]. Since such discrepancy was never observed for smaller molecules, this result can be attributed to the conformational structural change in the benzene molecule when it loses two electrons. The nuclear rearrangement in the transient period to the new geometry seems to make fragmentation more likely when a mass asymmetry is introduced in the system.

These results represent, therefore, a paradigm shift regarding the use of isotopic analogues for obtaining dication production cross sections for molecules with an even symmetry, in particular when a significant molecular geometry change occurs in the process. This selectivity should be investigated for other isotopically-substituted aromatic compounds.

References

[1] Märk T D 1975 *J. Chem. Phys.: Conf. Ser.* **63** 3731
[2] Wolff W *et al.* 2020 *J. Phys. Chem. A* **124** 9261
[3] Sigaud L and Montenegro E C 2020 *J. Phys.: Conf. Ser.* **1412** 052007
[4] Sigaud L, Wolff W and Montenegro E C 2022 *Phys. Rev. A* **105** 032816

---

[*] E-mail: lsigaud@id.uff.br