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Vacuum Ultraviolet Fingerprints as a New Way of Disentangling Tropylium/Benzylum Isomers

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Abstract

The two inseparable companions, tropylium (\mathbf{Tr}^+) and benzylum (\mathbf{Bz}^+), were interrogated by vacuum ultraviolet (VUV) radiation from 4.5 to 7.0 eV in an ion trap. These new fingerprints provide a new means of distinguishing these two C_7H_7^+ intertwined isomers. In particular, the singular spectral signature of \mathbf{Tr}^+ in the VUV consists of a single strong electronic transition at ≈ 6 eV. To illustrate this diagnostic tool, we shed light on the structure of the C_7H_7^+ intermediate that is ubiquitous when using commercial atmospheric pressure photoionization (APPI) sources. We have identified its structure as the 7-membered ring \mathbf{Tr}^+ , which contradicts some previous beliefs.

The structures and energies of C_7H_7^+ ions have intrigued chemists ever since Hückel predicted, in 1931, that aromatic molecules containing 6 π electrons, such as the tropylium-type

structure (\mathbf{Tr}^+), possessed extraordinary stability.¹ In addition to \mathbf{Tr}^+ , many other structures of C_7H_7^+ should exist.^{2,3} The second most stable is benzylium (\mathbf{Bz}^+) and consists of a toluene from which a hydrogen atom has been removed from the methyl group. The formation of the various isomers has perhaps been the most studied problem in gas-phase physical organic chemistry.⁴ Particular emphasis was placed on understanding the formation routes of the two most stable isomers, \mathbf{Tr}^+ and \mathbf{Bz}^+ , as well as their interconversion pathways, as evidenced by this non-exhaustive list of references, Refs. 4–22, contributing to this topic.

The formation of \mathbf{Tr}^+ *versus* \mathbf{Bz}^+ can be ascertained by their difference in reactivity.^{5,6} Indeed, \mathbf{Bz}^+ reacts readily with toluene *via* CH_2^+ transfer, whereas \mathbf{Tr}^+ is unreactive. They can also be identified by their characteristic spectral fingerprints, but only few spectroscopic data are available owing to the difficulty of efficiently and selectively producing \mathbf{Tr}^+ and \mathbf{Bz}^+ . Yet, the two isomers have been disentangled by their infrared (IR) spectra,^{19,20} but until recently only the gas-phase electronic spectrum (visible and ultraviolet) of \mathbf{Bz}^+ was available,^{23,24} preventing the use of electronic spectroscopy to distinguish \mathbf{Tr}^+ from \mathbf{Bz}^+ . The gas-phase electronic spectrum of \mathbf{Tr}^+ was finally recorded,²⁵ but showed only a weak symmetry-forbidden $S_1 \leftarrow S_0$ transition at $\approx 4.4\text{ eV}$ in the spectral range typically covered by tabletop lasers. This transition results from the Herzberg-Teller vibronic coupling between the S_1 and S_2 electronic states.^{25,26} The $S_1 \leftarrow S_0$ transition is therefore not the most appropriate target for \mathbf{Tr}^+ identification. However, the $S_2 \leftarrow S_0$ transition was expected to be strong (vertical excitation calculated at $\approx 6.4\text{ eV}$,²⁶ 6.1 eV ,²⁷ 6.7 eV ²⁵), making it a good target for probing the presence of \mathbf{Tr}^+ . Hence, this is the motivation of the present study.

We propose to use a linear ion-trap mass spectrometer coupled to a tunable vacuum ultraviolet (VUV) radiation source to perform VUV photodissociation action spectroscopy of C_7H_7^+ . This provides a new means of probing the population distribution of C_7H_7^+ isomers. In particular, the VUV photodissociation action spectrum of \mathbf{Tr}^+ will provide the first observation of its bright S_2 electronic state. This new tool is applied to unambiguously answer the question of the structure of the intermediate m/z 91, ubiquitously observed when

toluene is used as dopant in the commercial atmospheric photoionization sources (APPIs) widely used for analytical mass spectrometry.

Let’s start by establishing the diagnostic tool. Figure 1 shows the VUV photodissociation action spectra of **Bz**⁺ and **Tr**⁺ in panels a) and b), respectively. The experimental methodology is described in Section Methods.

Briefly, **Bz**⁺ was generated in an electrospray ionization (ESI) source from the benzyamine precursor, as was done by Féraud *et al.*²⁴ To establish that the spectral signature obtained in the VUV spectral range is indeed that of **Bz**⁺, its absorption spectrum was calculated using time-dependent density-functional theory (TDDFT), see Section Methods for details. Our calculation was shifted down by 1 eV, a value close to the shifts used in the work of Dryza *et al.* (−0.66 and −0.72 eV) which were necessary to adjust their calculations on their experimental spectra of the two lowest electronic transitions.²³ Note that Féraud *et al.*²⁴ recorded the UV spectrum of **Bz**⁺ up to 5.5 eV, their highest energy band observed is centered at 5.3 eV, which is also present in our spectrum. For all the above reasons, we are convinced that the experimental spectrum shown in panel a) of Figure 1 is the UV/VUV fingerprint of **Bz**⁺.

Tr⁺ was made from the tropylium tetrafluoroborate salt in an ESI source. The UV/VUV spectral signature of **Tr**⁺ can be seen in panel b) of Figure 1. The spectrum is relatively simple, consisting of a single electronic transition centered at ≈ 6 eV. Our TDDFT calculations predicts only one strong electronic transition at 5.98 eV in the energy range covered, as also predicted in previous studies.^{24–27} No shift of the calculated spectrum was needed to well reproduce the experimental spectrum. This experimental spectrum provides the first strong electronic spectral signature of **Tr**⁺, enabling a facile identification.

To illustrate the power of this new tool to easily disentangle **Tr**⁺ from **Bz**⁺, we decided to unveil the structure of the ion at m/z 91 that pervades in mass spectra when APPI sources are used with toluene as a dopent. For a complete overview of possible ion generation mechanisms in an APPI source, see Refs. 28–31. In brief, our APPI source uses a Kr lamp,

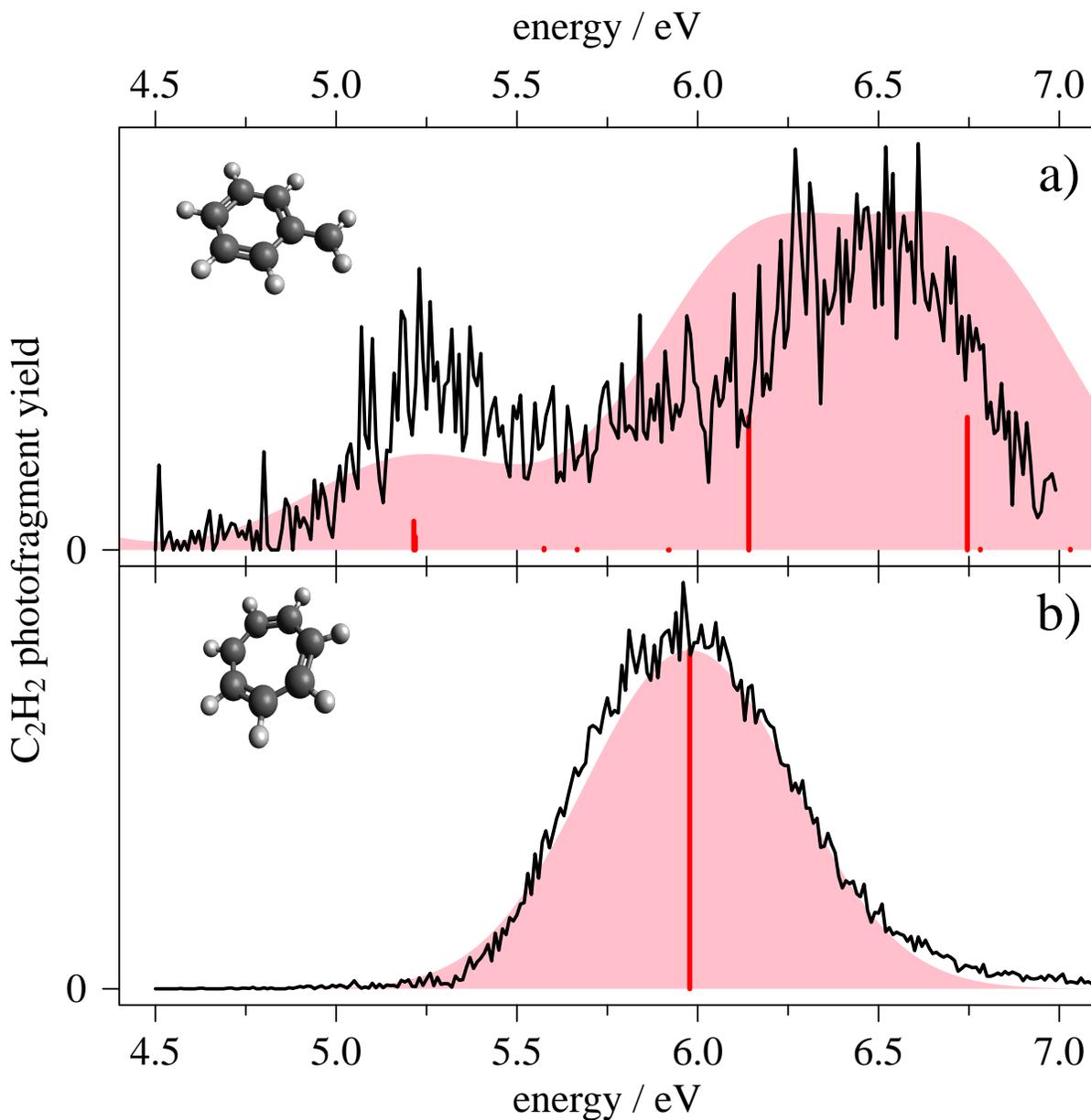


Figure 1: VUV photodissociation action spectra of **Bz⁺** (a) and **Tr⁺** (b) over the 4.5–7 eV range. The black traces are obtained by monitoring the loss of C₂H₂ (m/z 65). The red sticks correspond to the positions and intensities of the calculated vertical excitation. The shaded areas correspond to the convolution by Gaussian functions of the stick spectra using a full width at half-maximum of 0.36 eV.

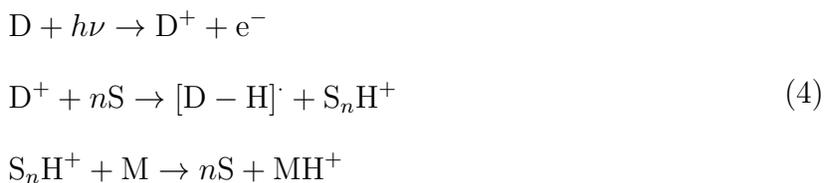
producing photons at 10.6 eV. The analyte (molecule of interest, M) can be directly ionized if its ionization energy is below 10.6 eV, as described in Eq. 1.



Ions can also be formed by charge transfer from a dopant (D) that is directly ionized as shown in Eq.2.



Finally, APPI can also protonate the analyte to form MH^+ , either by proton transfer with the dopant (Eq. 3) or with the solvent, S (Eq. 4).



In the case of toluene is used as a dopant, D^+ is $C_7H_8^+$ (m/z 92) and therefore $[D - H]^\cdot$ is the C_7H_7 radical that can either has the benzyl or the tropylium structure.³¹ Another study seems to favor the formation of benzyl radical based on proton affinity differences.²⁸ The fact that toluene cation can undergo hydrogen-atom loss to form $C_7H_7^+$ has been mentioned as a further complication in the interpretations of the mechanisms involved in APPI sources.

Yet, no studies have been carried out to elucidate the structure of the m/z 91 ion, although it has been postulated that it might be the \mathbf{Tr}^+ isomer.³⁰ Using our diagnostic tool, we were able to fingerprint this ion in the VUV spectral range and found that under different source conditions, low voltage applied on the source cone (10 V low activation) and high voltage (80 V, high activation), only the \mathbf{Tr}^+ structure was observed, as can be seen in Figure 2.

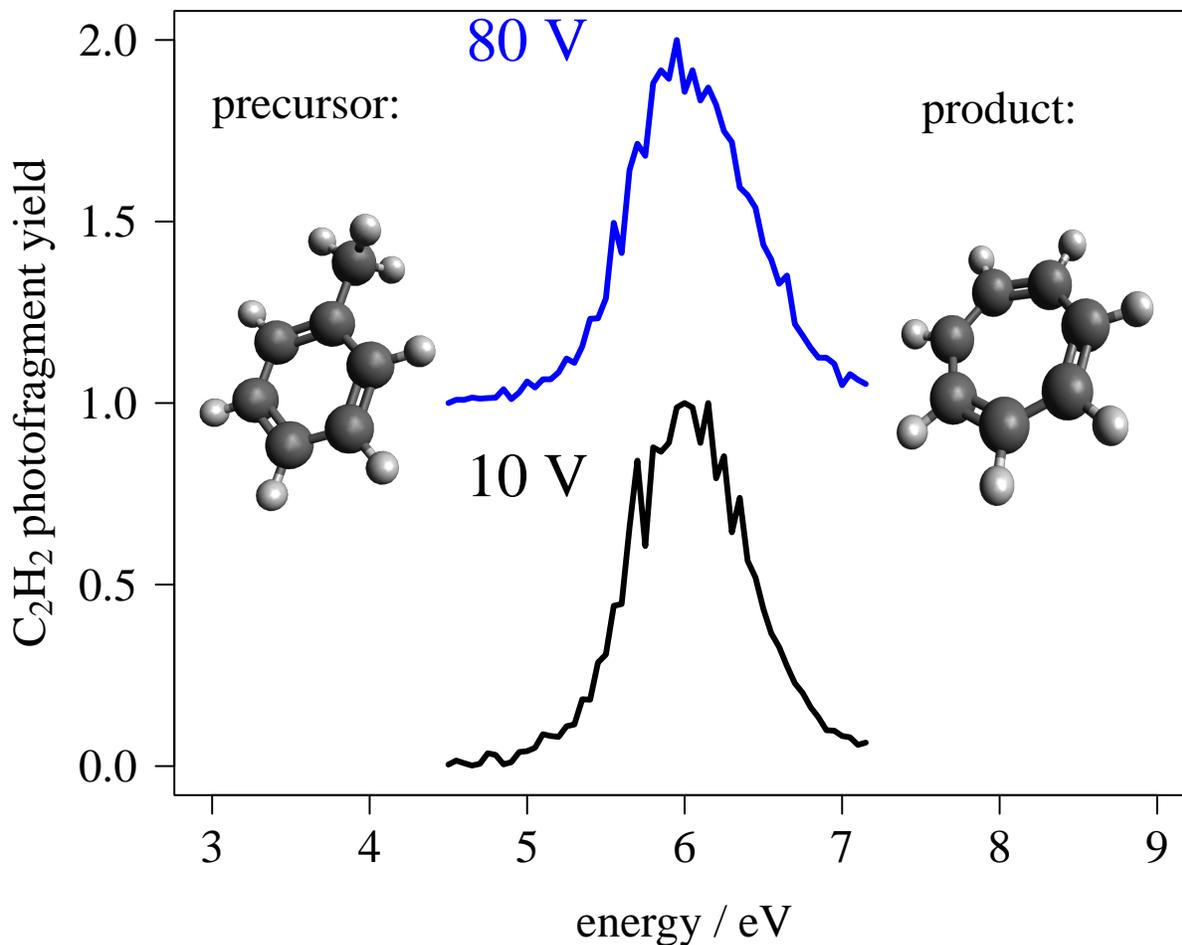


Figure 2: VUV photodissociation action spectra of m/z 91 originating from toluene using a cone voltage of 10 V and 80V for the black and blue traces, respectively.

Bodi and coworkers⁹ used imaging photoelectron photoion coincidence spectroscopy to investigate the structure of the C_7H_7^+ isomers formed upon dissociative single-photon ionization from toluene and cycloheptatriene. They found an appearance energy for \mathbf{Tr}^+ at \approx 11 eV under high-vacuum condition. This indicates that with a photon energy of 10.6 eV en-

ergy at atmospheric pressure, \mathbf{Tr}^+ cannot be formed by direct dissociative ionization process. Other routes of forming $\mathbf{C}_7\mathbf{H}_7^+$ come from their neutral counterparts. It seems unlikely that another photon from the lamp can ionize $\mathbf{C}_7\mathbf{H}_7$. However, as the IE of toluene (8.83 eV³²) is higher than that of tropylium (6.23 eV³³) and benzyl (7.25 eV)³⁴ radicals, $\mathbf{C}_7\mathbf{H}_7^+$ could be formed from charge transfer from the toluene cation.

In conclusion, we propose a new way of fingerprinting and thus disentangling the two most stable $\mathbf{C}_7\mathbf{H}_7^+$ isomers, \mathbf{Tr}^+ and \mathbf{Bz}^+ . The characteristic spectra features of each isomers are summarized in Table 1.

Table 1: Band maxima and their relative intensities for \mathbf{Tr}^+ and \mathbf{Bz}^+ .

Species	Band maxima / eV	Relative intensities
\mathbf{Tr}^+	6.0	1
\mathbf{Bz}^+	5.4	0.6
	5.8	0.5
	6.5	1

We took advantage of the fact that \mathbf{Tr}^+ has only one strong electronic transition center at 6 eV, giving it a peculiar and easily recognizable spectral signature. We applied this approach to elucidate the structure of the m/z 91 ion always present when toluene is used in APPI sources. We unveiled a 7-membered ring structure corresponding to the \mathbf{Tr}^+ species, which can either indicate that the long-standing belief that benzyl radical is formed during proton transfer reactions in APPI sources, when toluene is the dopant, is erroneous (at least within the explored experimental conditions), or that during the charge transfer reaction, a rapid and efficient conversion of \mathbf{Bz}^+ to \mathbf{Tr}^+ occurs.

Methods

Experimental: The photodissociation of $\mathbf{C}_7\mathbf{H}_7^+$ species following excitation with VUV light was studied using action spectroscopy with an LTQ linear ion trap coupled³⁵ to the DESIRS undulator-based VUV beamline³⁶ at the SOLEIL synchrotron facility in Saint-

Aubin (France). Samples were diluted at a concentration of 10^{-4} mol/L in solution of 50:50 methanol:water and 50:50 toluene:methanol when using the electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) sources, respectively. \mathbf{Tr}^+ was generated from tropylium tetrafluoroborate salt (97 % purchased from Thermo Scientific) using ESI in a MS² fashion (activation in the source). \mathbf{Bz}^+ was generated from benzylamine ($\geq 99\%$ purchased from Sigma-Aldrich) using ESI and APPI in a MS³ manner (*i.e.*, selection of the protonated benzylamine in the ion trap and then production of the \mathbf{Bz}^+ by knocking off the NH_3 group with collisions). To probe the m/z 91 formed during APPI experiments, only the solvent (50:50 toluene:methanol) was introduced. Once the desired m/z 91 ions were isolated, they were photoexcited by the synchrotron radiation in the VUV range from 4.5 to 7.0 eV in steps of 0.01 eV. A gas filter filled with Kr gas was used to prevent pollution from higher harmonics of the undulator synchrotron radiation in addition to a Suprasil window. The C_2H_2 photofragmentation yields were kept well below 10% by setting the irradiation time to 1 s to prevent multiple sequential one-photon absorption processes. The data processing of the recorded mass spectra was done using the MassJ package³⁷ written in the Julia language.³⁸ Photodissociation action spectra were corrected by the incident photon flux as measured by a calibrated VUV photodiode (IRD AXUV100), as detailed in Ref. 39.

Computational: Calculations were performed using the Gaussian 16 software suite.⁴⁰ Optimized geometries were searched using density-functional theory at the B3LYP/cc-pVDZ level of theory.⁴¹⁻⁴³ TD-DFT method⁴⁴ with the inclusion of 16 states at the B3LYP/cc-pVDZ level of theory was used to compute the absorption spectra of \mathbf{Bz}^+ and \mathbf{Tr}^+ .

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Author contributions: U. J. conceived the experiment. All authors performed the experiment. U. J. performed the calculations. All authors analyzed the data and wrote the manuscript. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** All data are available upon request from the corresponding author.

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