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Single and double ionization of the camphor molecule excited around the C 1s edge

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RATIONALE: An interesting class of volatile compounds, the monoterpenes, is present in some plants although their functions are not yet fully understood. We have studied the interaction of the camphor molecule with monochromatic high-energy photons (synchrotron radiation) using time-of-flight mass spectrometry and coincidence techniques.
METHODS: A commercial sample of S-camphor was admitted into the vacuum chamber, without purification, through an inlet system. Monochromatic light with energy around the C 1s edge was generated by the TGM beamline at the Brazilian Synchrotron Facility. A Wiley-McLaren mass spectrometer was used to characterize and detect the ions formed by the camphor photoionization. The data analysis was supported by energy calculations.
RESULTS: Although the fragmentation patterns were basically the same at 270 eV and 330 eV, it was observed that above the C 1s edge the contribution to the spectrum from lower mass/charge fragment ions increased, pointing to a higher degree of dissociation of the molecule. Projections of the PEPIPICO spectra demonstrated the existence of unstable doubly charged species. The Gibbs free energy was calculated using the Møller–Plesset perturbation theory (MP2) for the neutral, singly and doubly excited camphor molecule.
CONCLUSIONS: Our PEPIPICO spectrum clearly demonstrated the formation of doubly ionic dissociative species. From a slope analysis, we propose a secondary decay after a deferred charge separation mechanism in which, after a few steps, the camphor dication dissociates into $C_2H_3^+$ and $C_3H_5^+$. This is the main relaxation route observed at 270 eV and 330 eV. The large energy difference between the mono and the dication (of the order of 258.2 kcal/mol) may explain the experimentally observed absence of stable dications in the spectra, because their formation is disadvantaged energetically.

It is well established that molecular doubly charged ions are usually short-lived and highly reactive. The detailed characterization of their electronic structure and geometrical parameters is particularly challenging, from both theoretical and experimental points of view.[1] In standard electron ionization mass spectrometry, stable (at least in a few microseconds time scale) doubly charged ions are usually of low abundance (less than 1% of the base peak). Exceptions are found in the mass spectra of aromatic molecules (abundance as high as 20%) and other molecules containing conjugated systems, due to π-electrons.[2] Interestingly, many mass spectrometers currently used in organic analytical chemistry labs only report *m/z* values to the nearest integral mass, so that detecting ions at non-integral masses, such as the doubly (and multiply) charged molecular ion of a compound having an odd mass, is possible but the doubly or triply charged species are not usually properly assigned.[3] Irrespective of their usually lower abundances than monocations, doubly (and multiply) charged ions are considered to play a significant role in interstellar and ionospheric chemistry due to the interaction of matter with high-energy photons and charged particles. A fascinating aspect of the study of molecular dications is the

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very nature of their chemical stability (or instability). In other words, under which conditions would a doubly charged species overcome the positive charge repulsion? The balance between the electrostatic and chemical bonding forces seems to be extremely dependent on the size and on the electronic structure of the molecular ion.

In order to explore the stability of doubly charged molecular ions, we have undertaken a systematic study of the dissociation mechanisms of molecules excited at the valence and core levels, using synchrotron radiation and a photoelectron-photoion double coincidence technique, PEPICO, and a triple coincidence technique, photoelectron-photoion-photoion, PEPIPICO.[4,5]

In these techniques, detection of an electron gives rise to a start signal from which the times of arrival of the subsequent ions can be measured absolutely in a given time window.[6] For instance, in a previous study of the chloroform ($CHCl_3$) molecule, it has been demonstrated that stable and unstable doubly and triply charged ions are formed, following the ionization of the molecule around the Cl 2p edge.[7] Very recently, the single and double ionization of carvone, a volatile natural product, has been reported.[8] In the present paper we extend this type of analysis to a much larger compound, camphor, which has been subjected to the same experimental technique.

The structure of camphor molecule, at the ground level, is represented in Fig. 1. Camphor may be considered as a prototype for the study of the ionic fragmentation of bicyclic terpenes. The electron ionization induced fragmentation of this molecule has been studied previously.[9–13] As a chiral molecule, camphor has been the focus of recent circular dichroism studies.[14,15] The valence and C 1s core level ionization energies have also been previously determined. The ionization energy for the HOMO (carbonyl oxygen lone pair) is reported as 8.70 ± 0.05 eV, while for the core orbitals, the carbonyl C 1s ionization energy is 293.0 ± 0.01 eV and the remaining carbon atoms ionize at 290.5 ± 0.01 eV.[16–18]

In this first application of the PEPICO and PEPIPICO techniques to the camphor molecule excited around the C 1s edge we unambiguously show that ionization of the camphor molecule, both below and above the C 1s edge, results in the formation of unstable doubly charged species.

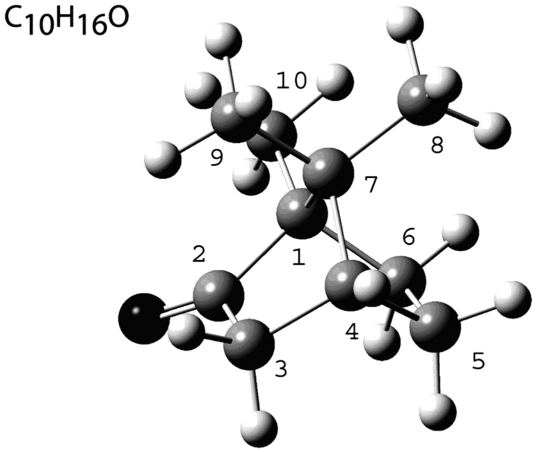

Figure 1. Structure of the camphor molecule optimized at the ground state.

Energy calculations have also been performed with the purpose of supporting the analysis on the dissociation of the camphor molecule.

EXPERIMENTAL

The experiment was performed at the Brazilian Synchrotron Light Laboratory (LNLS), in Campinas, Brazil. The experimental setup has been previously described in detail elsewhere.[19,20] Briefly, light from a toroidal grating monochromator (TGM) bending magnet beamline (12 to 330 eV) intersects the effusive vapor sample inside a high-vacuum chamber, with a base pressure in the 10^{-8} Torr range. During the experiment described here, the pressure was maintained below 10^{-5} Torr. The emergent photon beam was recorded by a light-sensitive diode.

Electrons resulting from the photofragmentation of the gaseous sample are accelerated in the direction of a set of micro-channel plate detectors, mounted in chevron configuration. The electrons are recorded without energy analysis. They provide the start signal to the time-to-digital converter (TDC). The produced cations are accelerated in the opposite direction to a time-of-flight (TOF) mass spectrometer, where they are detected by a second pair of micro-channel plate detectors. These ions produce stop signals to the TDC card.

The TOF spectrometer was designed in order to achieve 100% efficiency for cations with kinetic energies up to 30 eV and electrons with kinetic energies up to 150 eV, without angular discrimination.[21] The sample of S-camphor, 95%, was purchased from Sigma-Aldrich (St. Louis, MO, USA) and was used without further purification. An inlet system was used to admit the sublimating sample into the vacuum chamber. It was not necessary to heat the inlet system due to the high vapor pressure of the sample.

Calculations

In order to investigate the thermodynamics parameters of the camphor dication and its route for dissociation, Gibbs free energy theoretical calculations were carried out with the Gaussian 98 package.[22] All transition state structures, intermediates and precursors involved were fully optimized by density functional theory (DFT).[23,24] Energy profiles at selected DFT geometries along the reaction pathway were computed at the MP2 level of theory using a 6-31+G(d,p) basis set. For all the different calculation methods, the algorithms conjugate gradient and quasi-Newton-Raphson were used for the geometry optimization until a gradient of 10^{-9} atomic units was obtained. The final geometries were obtained with DFT using the Becke's three parameter hybrid functional with the LYP correlation functional.[25] The final structures were submitted to analysis of Natural Bond Order (NBO)[26] with the density functional B3LYP using the basis set 6-311+G**.[27] This computational procedure has been employed previously on similar systems with success.[28–30] The Wiberg indices were also calculated at the B3LYP/6-311+G** level. Furthermore, after each optimization, the nature of each stationary point was established by calculating and diagonalizing the Hessian matrix (force constant matrix). The unique imaginary frequency associated with the transition vector (TV),[31] i.e., the eigenvector associated with the unique negative eigenvalue of the force constant matrix, was characterized.

RESULTS

Mass spectra for the camphor molecule measured in the PEPICO mode have been obtained both below (270 eV) and above (330 eV) the C1s edge and these are shown in Figs. 2 and 3, respectively. Assignments and relative intensities (normalized to intensity of the molecular ion, *m/z* 152) for the main fragment ions observed at these two energies are presented in Table 1. For the sake of comparison, we have also included in Table 1 the main fragment ions and respective intensities as observed in the standard electron ionization mass spectrum for this molecule.[32] In order to search for doubly (or multiply) ionized species, PEPIPICO spectra have also been obtained at the same photon energies. The coincidence map obtained at 330 eV photon energy, corrected for false events, is shown in Fig. 4, and the coincidences, projected on the T1 and T2 axes, are presented in Fig. 5. For a given ion pair, the time of arrival of the first ion is registered at T1, while the time of arrival of the second ion is registered at T2. We see a large contribution from H^+,

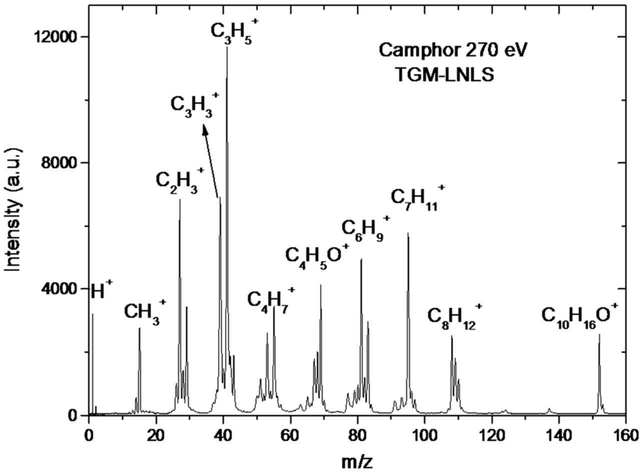

Figure 2. Mass spectrum of the camphor molecule obtained at 270 eV (TGM = Toroidal Grade Monochromator, LNLS = Brazilian Sychrotron Light Laboratory).

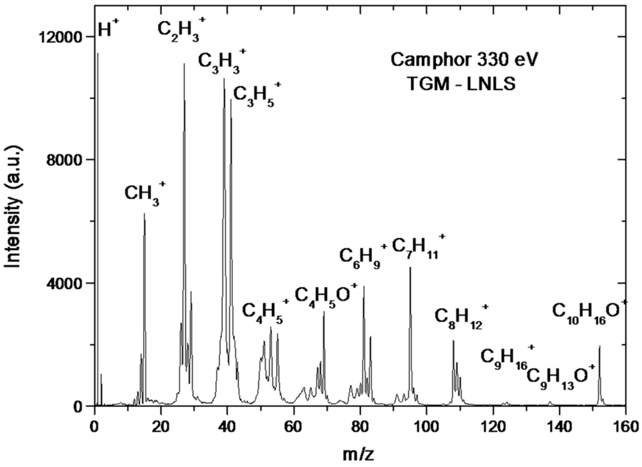

Figure 3. Mass spectrum of the camphor molecule obtained at 330 eV (TGM = Toroidal Grade Monochromator, LNLS = Brazilian Sychrotron Light Laboratory).

Table 1. Relative intensities (branching ratios) of the fragment ions of the camphor molecule excited by photons (270 eV and 330 eV) and electrons (70 eV). The associated error is around 10%

		Ion yield*		
		Electron ionization	Synchrotron radiation	
m/z	Assignment	70 eV	270 eV	330 eV
1	H^+	-	1.47	9.75
14	CH_2^+	-	0.50	2.37
15	CH_3^+	-	2.99	12.98
26	$C_2H_2^+$	-	0.88	4.14
27	$C_2H_3^+$	1.24	4.87	15.98
28	CO^+	-	1.21	2.37
29	HCO^+	-	2.27	4.69
37	C_3H^+	-	0.17	2.50
38	$C_3H_2^+$	-	0.18	6.81
39	$C_3H_3^+$	1.18	4.84	19.17
40	$C_3H_4^+$	-	0.12	4.63
41	$C_3H_5^+$	2.86	6.10	12.54
42	$C_2H_2O^+$	-	1.39	7.98
50	$C_4H_2^+$	-	0.60	4.12
53	$C_4H_5^+$	-	1.59	3.14
55	$C_4H_7^+$	1.37	1.97	2.79
69	$C_4H_5O^+$	1.39	1.57	1.94
81	$C_6H_9^+$	2.66	2.18	2.98
83	$C_6H_{11}^+$	1.19	1.33	1.77
95	$C_7H_{11}^+$	3.60	2.45	3.46
108	$C_8H_{12}^+$	1.40	0.95	1.43
109	$C_8H_{13}^+$	-	0.86	1.31
152	$C_{10}H_{16}O^+$	1.00	1.00	1.00

*The normalization was performed at *m/z* 152.

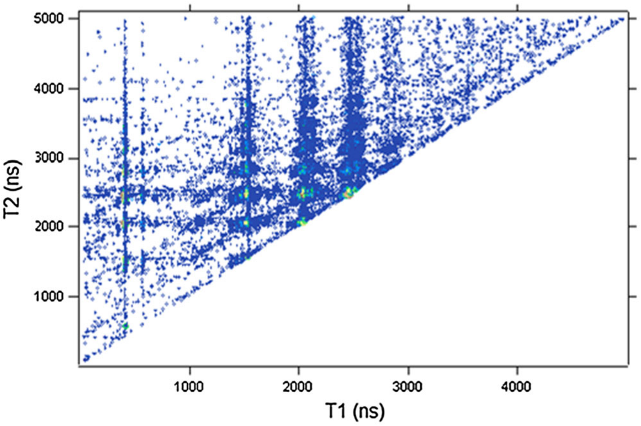

Figure 4. Coincidence map or PEPIPICO spectrum taken at 330 eV where T1 is the arrival time of the fastest ion and T2 is the arrival time of the second (slowest) ion. The ions are said to be in coincidence if they arrive at a previously defined time window.

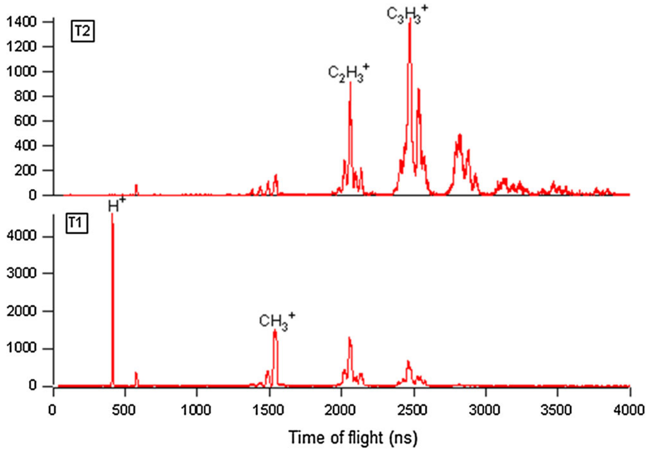

Figure 5. Projection of the PEPIPICO spectrum taken at 330 eV showing the time of flight of the most intense cations.

CH_3^+, $C_2H_3^+$ and $C_3H_3^+$ ions. The PEPIPICO spectrum clearly demonstrates the existence of unstable doubly ionized species. A slope analysis of the coincidence map of the PEPIPICO spectrum for each coincidence pair might help in the elucidation of the dication dissociation dynamics.

Data treatment

The areas of the peaks in the PEPICO and PEPIPICO spectra reflect, respectively, the relative abundance of each ionic species, in the first case, and of a given ionic pair, in the second case. However, before performing a complete description of the ionization process, it is necessary to correct the data for false and aborted coincidences. False coincidences are observed mainly when ions that are not correlated with the electron that originated the start of the experiment are detected. In these situations the ions appear in the PEPICO and PEPIPICO spectra in random positions, and can be easily excluded from the analysis. In the PEPIPICO spectrum, as a rule we exclude all the coincidences with only one count. Aborted coincidences, which occur when more ions are produced but not all of them are detected, are more difficult to identify and to correct for. These occur because the detection efficiency is not unitary. When this happens, the detected ions are summed up in the wrong coincidence spectrum. For instance, in the camphor spectrum the ion pair $C_2H_3^+ + C_3H_3^+$ is observed as the most intense coincidence. When we fail to detect one of these ions the other will appear in the PEPICO spectrum, instead of in the PEPIPICO spectrum. In order to correct for these aborted coincidences the detector efficiencies must be taken into account. A detailed explanation of the procedure followed can be found elsewhere.[5] Once all the corrections are made, the relative intensities can be obtained for all the excitation decay processes observed.

DISCUSSION

From Figs. 2 and 3 and Table 1 it can be seen that, irrespective of the photon energy, basically the same fragmentation pattern is observed in the mass spectra of the camphor molecule. Significant differences between individual spectra are essentially related to the relative intensities of the fragment ions. The three most intense fragment ions observed in the electron ionization (EI) mass spectra correspond, in decreasing intensity order, to *m/z* 95 (base peak), 41 and 81, which are assigned respectively to $C_7H_{11}^+$, $C_3H_5^+$ and $C_6H_9^+$. The base peak is considered to be associated with the loss of ketene (C_2H_2O) from the molecular ion followed by the additional loss of a methyl group. Other important fragment ions are observed at *m/z* 108, 83, 69 and 55. The dissociation mechanisms associated with the EI formation of these cations has previously been elucidated.[10–12] Doubly charged fragment ions are not often assigned, however, in EI spectra. In the typical energy range of 50–100 eV, single ionization processes that involve the outermost valence orbitals usually dominate EI mass spectra. Although double ionization may also occur, the cross sections for single ionization are usually much larger and as a result these processes dominate the mass spectra.

At 270 eV photon energy, as shown in Fig. 2 and listed in Table 1, the same fragment ions as appear in the EI studies are observed. However, now the three most intense ions are *m/z* 41 ($C_3H_5^+$), 27 ($C_2H_3^+$) and 39 ($C_3H_3^+$), in decreasing intensity order. Previously unreported fragment ions can, in addition, be seen at *m/z* 15 (CH_3^+) and 1 (H^+). The first valence ionization energy for the camphor molecule is 8.70 eV.[17,18] According to the empirical rules of Tsai and Eland[33] and of Kingston *et al.*,[34] the second and triple ionization energies are expected to occur, respectively, at approximately 26 eV and 43 eV. Contributions from double and triple ionization processes to the molecular mass spectrum taken at photon energies near the C 1s edge are consequently expected to occur.

It should be taken into consideration that, at a photon energy of 270 eV, core excitation is not expected to occur (the C 1s ionization energies are 290 eV for skeletal carbon atoms and 293 eV for the carbon atom directly bonded to the oxygen atom).[18] The observation of double (and multiple) ionization processes must consequently result from the direct absorption of a single photon. As these processes are forbidden in a single particle approximation, observation of doubly or multiply charged ionic species becomes, in this sense, a measure of the importance of electronic correlation processes in the photoexcited camphor molecule.

At 330 eV photon energy, the molecule can also undergo core (C 1s) ionization. Following a core electron ejection, very efficient double (or triple) ionization processes may come into play: a valence electron fills the core hole while another electron is ejected (Auger decay). There is also a smaller probability that two electrons may be ejected (double Auger decay). From Figs. 2 and 3 and Table 1, it can be seen that at 330 eV essentially the same fragmentation pattern is obtained as was observed at 270 eV, but with a much larger contribution to the spectrum from low-mass fragment ions such as H^+, CH_3^+, $C_2H_3^+$ and $C_3H_4^+$. In fact, the three most intense fragment ions in the 330 eV mass spectrum are at *m/z* 39, 27 and 15. This pattern clearly points to a much larger degree of fragmentation of the molecule following core ionization.

Stable (at least in the microseconds scale) doubly (or triply) charged species remain unobserved in the mass spectra obtained at 270 eV and 330 eV. Definite evidence for the formation of (dissociative) dications at both photon energies may nonetheless be obtained from our PEPIPICO data, as shown in Figs. 4 and 5. At 270 eV (spectrum not shown), the most significant pairs of ions observed were ($C_2H_3^+/C_3H_3^+$) and ($C_3H_3^+/C_3H_5^+$). At 330 eV, the predominant pairs were ($C_2H_3^+/C_3H_3^+$) and ($CH_3^+/C_3H_3^+$). An increase was observed in the intensity of the double coincidences when moving from 270 eV to 330 eV. The ($CH_3^+/C_2H_3^+$) and ($C_2H_3^+/C_3H_5^+$) coincidences were also observed at both photon energies.

Each ionic pair in the PEPIPICO spectrum results from a coulombic explosion of the doubly ionized molecule, when the electrostatic forces overwhelm the chemical ones. The absence of detectable stable dications in the PEPICO spectra may reflect a low structural and energetic stability for these ions. On the other hand, the PEPIPICO spectra show that dications are indeed formed. Consequently, we can infer that the camphor dications have very short lifetimes and may undergo a fast dissociation. Therefore, the dications are not seen in the PEPICO spectra.

In order to shed some light on the instability of the camphor dications, the Wiberg bond order indices were computed by using Natural Bond Orbital analysis. The resulting Wiberg indices for the neutral, singly charged and doubly charged camphor molecule are presented in Table 2 and Fig. 6. It is known that the Wiberg index is proportional to the bond strength. From our calculations, good agreement between the calculated and experimental geometry for neutral camphor[35] was observed. The Wiberg indices for the neutral form of camphor are very close to each other, ranging from 0.8107 to 0.8563, a clear indication of the similarity in the strength of all the bonds. Both the dication and the monocation, on the other hand, show a very small Wiberg index for the C_1–C_2 bond, pointing to the high probability of rupture of this bond during dication formation (Table 2).

The Gibbs free energy has also been calculated for the neutral, singly charged and doubly charged molecule using the MP/6-31+G(d,p) approximation, and the results are shown in Table 3. All discussions concerning the energy differences and the energy barriers refer to the enthalpy term, corrected for the zero point energy at 298.15 K. A ΔG difference of 258.2 kcal.mol^{-1} is observed between the monocation and dication forms. This large difference could also, in principle, be related to the absence of doubly charged fragment ions in the mass spectra, as they should be very unstable.

Based on our results, an interesting question can be formulated: what is the favorite route for the dissociation of the camphor dication? A reasonable answer may be obtained by energy calculations (free energy for the dication formation and the Wiberg indices) and applying the slope analysis of Simon *et al.*[5] There is a correlation of the slope of the PEPIPICO graph (determined by linear regression) with the dissociation dynamics of the dications. Figure 7 shows the intensity of the coincidence of the pair $C_2H_3^+/C_3H_3^+$ at 330 eV (the spectrum is quite similar to that at 270 eV). A linear regression was applied to the data and a value of −1.07 ± 0.06 was obtained for the best straight line. Based on the methodology proposed by Simon *et al.*,[5] we propose that the formation of the pair $C_2H_3^+/C_3H_3^+$ results from a secondary decay after deferred charge separation as follows:

$$C_{10}H_{16}O^{2+} \rightarrow C_5H_8^{2+} + C_5H_8O$$
$$C_5H_8^{2+} \rightarrow C_2H_5^+ + C_3H_3^+$$
$$C_2H_5^+ \rightarrow C_2H_3^+ + H_2$$

Trying to rationalize these reaction steps, a concise mechanism is proposed in Fig. 8. Our calculations have shown that core ionization leads to the breakage of the C1–C2 bond (Table 2). To counteract the electrostatic repulsion, a rearrangement is proposed involving the migration of a methyl group from C7 to the C2 positions, leading to a positive charge at C7. The next step involves cleavage of the C4–C7 and C5–C6 bonds, resulting in a double-bond formation between C4 and C5, releasing the neutral C_5H_8O. The dication $C_5H_8^{2+}$ then dissociates into $C_2H_5^+$ and $C_3H_3^+$. Finally, the $C_2H_5^+$ ion releases neutral H_2 to produce the $C_2H_3^+$ ion.

The observed similarity between the electron ionization and the high photon energy mass spectra deserves additional comments. As mentioned before, 70 eV EI mass spectra are usually dominated by cations associated with the single ionization of valence electrons. Double (and sometimes triple) ionization is energetically accessible, but the corresponding cross sections are usually small. At high photon energies, double ionization, although forbidden in a single particle approximation, is observed. The fact that the same fragment ions are observed using 70 eV electrons and 270 eV photons probably means that either the double ionization cross sections are still quite small at this photon energy or that the doubly ionized states decay very rapidly to singly ionized states through the fragmentation of the molecular ion. Cederbaum and collaborators have shown that there is an extremely high density of states associated with the double ionization of large molecules.[36–39] The doubly ionized final states would in general be highly dissociative and have a very short lifetime. It has also been pointed out very recently[40] that, for excited states which tend to be energetically close to each other, the Born-Oppenheimer Approximation (B–O) does not hold. As one of the consequences of the breakdown of the B–O approximation, surface crossings or conical intersections can lead to extremely fast radiationless decay of the photoexcited molecules.[40] We believe that a very fast decay from doubly to singly ionized electronic states may be an important reason for the observed similarity between the different mass spectra (270 eV and 330 eV).

A more careful comparison between the mass spectra obtained with (330 eV) and without (270 eV) participation of Auger processes shows that basically exactly the same

Table 2. Wiberg bond indices for dication, monocation and neutral camphor molecule at the B3LYP/6-311+G** level

Camphor form	C1–C2	C1–C10	C2–C3	C3–C4	C4-C5	C5–C6	C6–C1	C7–C8	C7–C9
Neutral	0.8634	0.8653	0.8642	0.8221	0.8274	0.8052	0.8107	0.8568	0.8530
Monocation	0.2128	0.0025	0.2539	0.2479	0.2491	0.2504	0.2460	0.2468	0.2500
Dication	0.0004	1.1622	1.1757	0.9433	1.0011	1.0054	1.1272	0.8517	0.9905

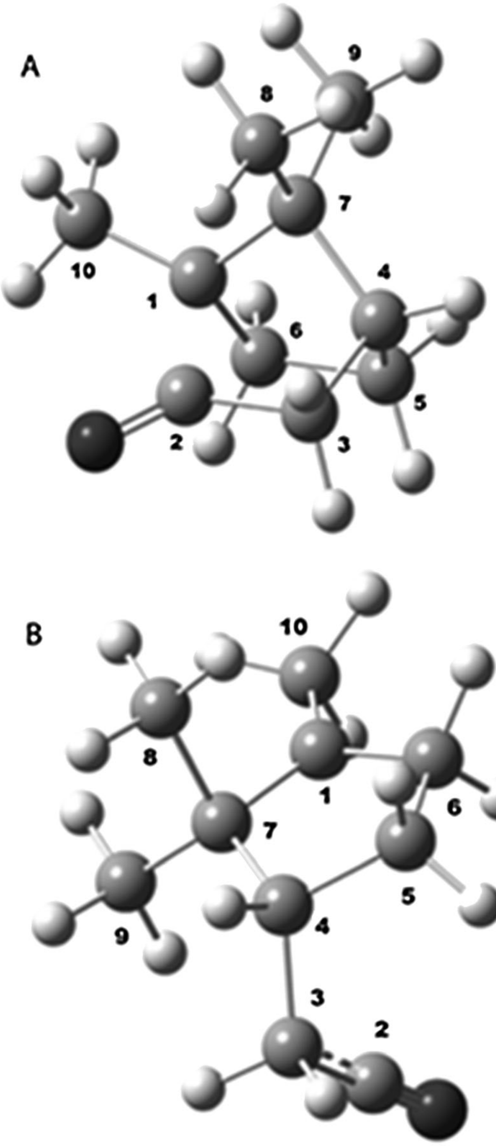

Figure 6. Optimized structures for the camphor monocation (A) and dication (B) obtained through DFT methodology.

Table 3. Gibbs free energy of monocation, dication and neutral camphor molecule using MP2/6-31+G(d,p)

Camphor molecule	ΔG (kcal.mol^{-1})
Dication	+446.1
Monocation	+187.9
Neutral	0.0

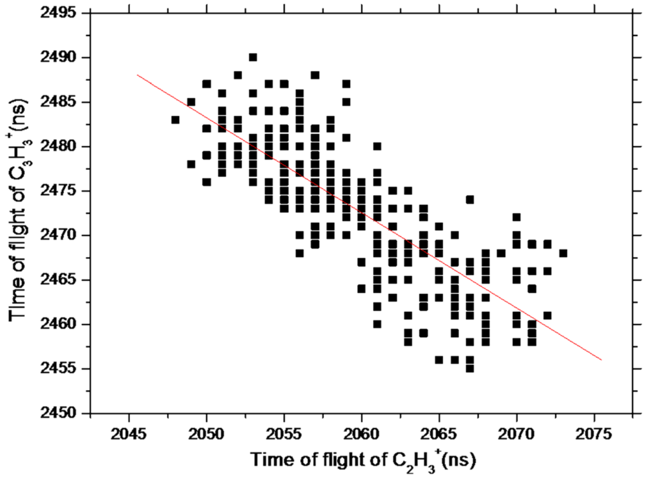

Figure 7. PEPIPICO spectrum of the ionic pair $C_2H_3^+/C_3H_3^+$.

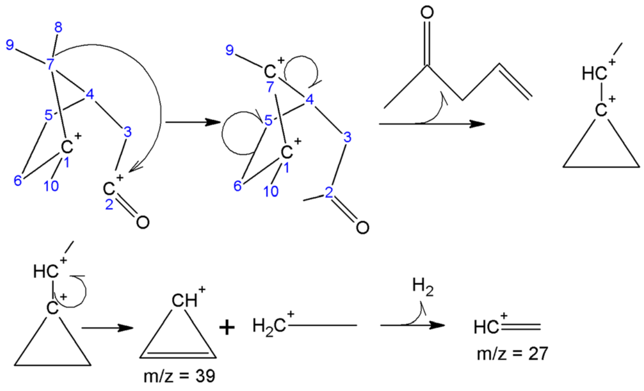

Figure 8. The proposed coherent mechanism for camphor dication decay leading to the formation of the ionic pair $C_2H_3^+/C_3H_3^+$.

fragment ions are formed in both cases. This demonstrates again that essentially the same final states are reached at these two photon energies. Auger decay is usually associated with a Coulomb explosion, related to the charge repulsion in a doubly charged ion. Following the Coulomb explosion, the ionic species are ejected with large kinetic energy values and this translates into a peak broadening in the TOF mass spectrum. Coulomb repulsion is expected to decrease with the size of the molecule and in the absence of double charge localization in a specific molecular site. This seems to be observed in the present case, considering the similarity between the mass spectra obtained at 270 eV and 330 eV and the absence of any peak broadening at the highest photon energy.

CONCLUSIONS

The ionic fragmentation of the camphor molecule, excited below (270 eV) and above (330 eV) the C 1s edge, has been studied for the first time using synchrotron radiation and electron-ion (PEPICO), electron-ion-ion (PEPIPICO) coincidence techniques. At these high photon energies double and triple ionization are both expected to play a role in the fragmentation of the molecule, particularly above the core edge, where Auger processes are considered quite efficient. The observed mass spectra present nonetheless a striking similarity, with basically the same fragment ions being observed in both cases. This similarity is discussed in terms of a suggested fast decay from the doubly excited states to the singly ionized states from which the molecule dissociates. The most intense ion pair coincidence in the PEPIPICO spectrum, both at 270 and at 330 eV, involves the $C_2H_3^+$ and $C_3H_3^+$ cations and is likely to occur through secondary decay following deferred charge separation. A fragmentation mechanism has been proposed, supported by calculations (the Wiberg indices show the weakest bonds) and slope analysis of the PEPIPICO spectrum. Our results suggest that the relaxations routes for the camphor dication involves principally the release of the neutral C_5H_8O and the $C_5H_8^{2+}$ dication, as well as the formation of cations with lower *m/z* values. Calculations of the Gibbs free energy and of the Wiberg indices, at DFT and MP2 levels, show a large difference between the neutral, singly charged and doubly charged camphor molecule, justifying, in principle, the absence of doubly charged fragment ions in the mass spectra, as they are very unstable.

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