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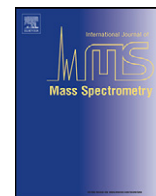


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Atmospheric pressure photoionization mass spectrometry of guanine using tunable synchrotron VUV radiation

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ABSTRACT

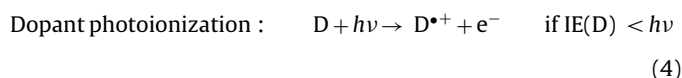
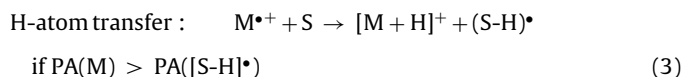
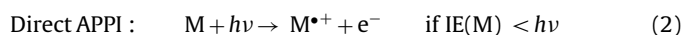
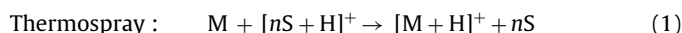
Atmospheric pressure photoionization (APPI) source coupled to a krypton discharge lamp permits to specifically generate either radical cation or protonated species for guanine depending on the dopant molecule. In order to scrutinize the consecutive or competitive chemical reactions occurring in the gas phase, a tunable synchrotron VUV radiation source was coupled for the first time to the APPI source of a hybrid quadrupole time-of-flight mass spectrometer. Experiments were achieved at different photon energies close to the ionization energy of the different reagents. This unique set-up allowed the confirmation of theoretical models developed by several groups over the last ten years concerning ionization processes underlying APPI, such as proton or charge transfer reactions.

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1. Introduction

Photoionization can be defined as the interaction between an electromagnetic radiation and matter, resulting in the production of an electron and an ion. Two main groups can be distinguished within the scientific community of photoionization users. The largest one is composed of physical chemists interested in the interaction between photons from tunable UV sources and molecular beams in order to precisely determine some physical parameters, such as the vertical or adiabatic ionization energies (IEs) [1–3]. Several interfaces have been introduced for the particular studies of combustion processes [4] or aerosol chemistry [5]. Such types of experiments are performed under reduced gas pressure in order to generate in the gas phase isolated molecules or small clusters. The second group is composed of analytical chemists who are mostly interested in the production of intense beams of molecular or fragment ions for quantitative or structural mass spectrometry, using an atmospheric pressure photoionization (APPI) source. In that case, ions are generated thanks to the interaction between UV photons from a gas-discharge lamp and a molecular beam produced by a thermospray probe and containing solvent, analyte and dopant

species [6–12]. Dopant species are chosen for their low IE to mediate in the ionization when direct photoionization of the analytes is poor. It must be noted that the mean free path of ions is only 65 nm at atmospheric pressure, meaning that a large amount of collisions occurs between the photoionization region and the entrance of the mass spectrometer. Guanine was previously used as a model compound for the study of chemical reactions involved in the APPI process when a krypton discharge lamp is used [9]. This lamp generates two emission lines, the most intense one at energy of 10.0 eV with a minor contribution at 10.6 eV. When anisole was used as a dopant, the signal intensities of the molecular ion $M^{\bullet+}$ and of the protonated molecule $[M+H]^+$ were mostly equal whereas only $[M+H]^+$ ion signal was detected in the absence of this dopant. The formation of these two ion species was rationalized according to the following chemical equations [6,9,13]:



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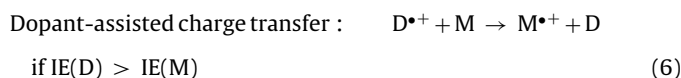
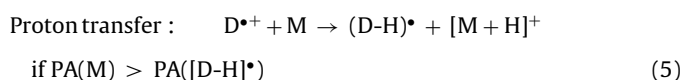
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Table 1

Ionization energies (IE) and proton affinities (PA) of the nucleobases and dopant molecules.

Compounds	IE (eV)	PA (kJ mol ⁻¹)
Water	12.62	691.0
Water dimer		816
Water trimer	10.84	862
Water tetramer		900
Methanol	8.1 ± 0.2	754.3
Methanol dimer		883
Methanol trimer		937
Guanine		959.5
Toluene	8.83	
Benzyl radical		831.4
Anisole	8.20	
Methoxyphenyl radical		~880

Data from NIST database (<http://webbook.nist.gov/chemistry/>) except for the proton affinity of the methoxyphenyl radical from Ref. [28] and of water/methanol multimers from Ref. [3].



where M corresponds to the molecule of interest, S to the solvent, D to the dopant, PA to the proton affinity and IE to the ionization energy.

According to the respective IE and PA values of guanine, methanol and water reported in Table 1, reactions (1)–(3) should occur even without the presence of dopant. Reaction (1) corresponds to a pure thermospray process which always exists due to the instrumental configuration of the commercial APPI source. The direct photoionization of the analyte in reaction (2) can occur if its IE is smaller than the photon energy. This reaction can be followed or not by a hydrogen atom transfer depending on the relative proton affinities of the analytes and the solvent molecules. When adding a dopant, reactions (4)–(6) can then become effective. Reaction (4) reflects the direct photoionization of the dopant which happens when the ionization energy of the dopant is lower than the photon energy. The two competitive reactions (5) and (6) can then arise depending on the thermochemical properties of the dopant and of the analyte. This model was built according to the limited experimental results using photons at two fixed energies (10.0 and 10.6 eV) only. Even if other discharge lamps, such as those using xenon (8.4 eV) or argon (11.7 eV), can be used to replace the krypton one in commercial APPI sources, it would remain difficult to validate the above model with only 3 experimental data points. In this model it was also assumed that all the ionization reactions were occurring in the gas phase. As far as we know, there is no study which clearly describes the physical state of chemical compounds under the irradiation of a discharge lamp, i.e. a pure gas phase, a micro-solvated environment or even liquid droplets. Then in order to better understand the physico-chemical mechanisms involved by APPI, a tunable UV source, i.e. the DISCO beamline [14] at the SOLEIL synchrotron radiation facility was coupled to a Photospray® APPI source on a commercial hybrid quadrupole-time-of-flight mass spectrometer [15]. This unique instrument is thus able to measure at atmospheric pressure ion formation thresholds as a function of the photon energy. The behavior of guanine under different experimental conditions, with or without dopant molecules, was chosen as a first case study to demonstrate the efficiency of this new set-up, in order to put side by side the previously postulated mechanism to the present experimental results.

2. Experimental methods

2.1. Chemicals and reagents

High-performance liquid chromatography (HPLC) grade methanol was purchased from Baker (Deventer, Netherlands), water was *in-house*-bidistilled and filtered on Millipore cartridges and anisole (99% purity) purchased from Acros Organics (Geel, Belgium). Guanine was purchased from Sigma–Aldrich (Saint-Quentin-Fallavier, France). Ion-exchange resins (Amberlite IR-120 Plus, Inc., Ohio, USA) were added in order to reduce the signal intensity of sodium cationized species.

2.2. Mass spectrometry

All the experiments were performed at the DISCO beamline [14] of the SOLEIL synchrotron radiation facility (Gif-sur-Yvette, France). VUV photons were selected with a monochromator of which wavelength resolving power was ranging from 875 at 60 nm to 2700 at 180 nm [15]. The beamline was maintained under a high vacuum (1×10^{-9} hPa) and separated by an MgF₂ window from the atmospheric pressure photoionization source. The photons were driven toward the APPI source exactly where the photons were emitted by the discharge lamp of the commercial Photospray® source (AB Sciex, Toronto, Canada) [15,16]. The photon transmission through the differential pumping system was comprised between 80 and 100% for photon energies ranging between 7 and 9 eV [17]. The source was finally coupled to a hybrid quadrupole-time-of-flight mass spectrometer (QStar, AB Sciex).

The samples were introduced using the flow-injection analysis (FIA) method: 20 µL of the sample solution at 10^{-6} mol L⁻¹ were loaded into an injection loop and pushed through the APPI source by the solvent (MeOH/H₂O, 50/50, v/v) at a flow rate of 400 µL min⁻¹. The dopant was added by an auxiliary capillary at a flow rate of 1 µL min⁻¹. These experimental conditions were optimized to generate the largest amount of M^{•+} ion species when using anisole as a dopant. The experimental errors with an ion counting system can be estimated by using the following formula:

$$\text{Experimental error} = \frac{N}{\sqrt{N}},$$

with *N* being the number of counts.

The mass spectrometer instrumental parameters were adjusted in order to obtain the best signal-to-noise ratio and to minimize in-source collision-induced dissociation (CID). The operating parameters for guanine were: ion source voltage (ISV) 1200 V, declustering potential 1 (DP₁) 20 V, focusing potential (FP) 100 V, and declustering potential 2 (DP₂) 15 V. The chemical background induced by the solvent was systemically removed by subtracting the mean signal acquired during 20 s before each injection.

3. Results and discussion

The mass spectrum of guanine recorded at 450 °C in water/methanol (50/50, v/v) under synchrotron radiation atmospheric pressure photoionization (SR-APPI) conditions with 8.0 eV UV photons is shown in Fig. 1. Intense peaks assigned to [M+H]⁺ (*m/z* 152) and [M+Na]⁺ (*m/z* 174) ions are detected. The addition of Amberlite™ resins to the sample was inefficient to remove the sodium adduct peak, because guanine exhibits a high sodium affinity [18]. The sodium-cationized species observed under such conditions are produced by a thermospray like process that can be considered as desolvation of charged species preformed in solution, as shown in previous works [19]. Indeed, whatever the photon energy, the signal intensity of the [M+Na]⁺ ion did not vary at all. Fig. 2 shows the variations of the [M+H]⁺ ion abundance as a

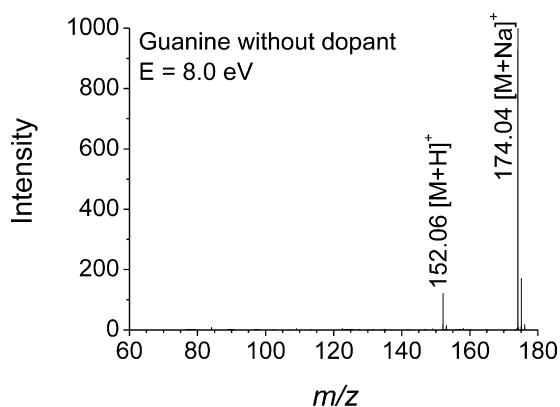


Fig. 1. SR-APPI mass spectrum of guanine recorded at 450 °C in H₂O/CH₃OH (50/50, v/v) without dopant and with 8.0 eV energy photons.

function of the photon energy. A plateau is first observed below ~8.15 eV, followed by a linear increase for photon energies above this value (slope: 22.2 ± 1.0 counts/eV). With photon energy lower than the IE of guanine, the corresponding [M+H]⁺ ion signal is simply due to the thermospray process (reaction (1)) as for [M+Na]⁺. The thermospray mechanism has been largely described by the group of Vestal [20]. The first step is the formation of a superheated mist transported in a supersonic vapor jet. Due to their low volatility, the biological molecules are mostly retained in the droplets of the mist. According to the model developed by Dole, the droplets are randomly positively or negatively charged. Solvent molecules are then removed from the superheated charged droplets, leading to Coulomb explosions and field desorption of small clusters of molecular ions and solvent. The size of these clusters depends on the pressure and the temperature of the vapor in the ion source. Here some ion/molecule reactions can occur depending on their exothermicity. In the present case, guanine exhibits a significantly higher proton affinity than small water or methanol clusters (Table 1), which prevents it to be deprotonated by the solvent. It was also assumed that solvent clusters could play a role in the APPI process when using a krypton discharge lamp [21]. However, since the threshold energies of protonated water, methanol or water/methanol clusters were all measured between 9.6 and 10.2 eV [3], and since the present experiments were all done with photon energies below 9.0 eV, the photoionization of solvent clusters will not be considered in the following.

With photons of energy above 8.15 eV, guanine is firstly photoionized (reaction (2)), leading to transient radical ions which

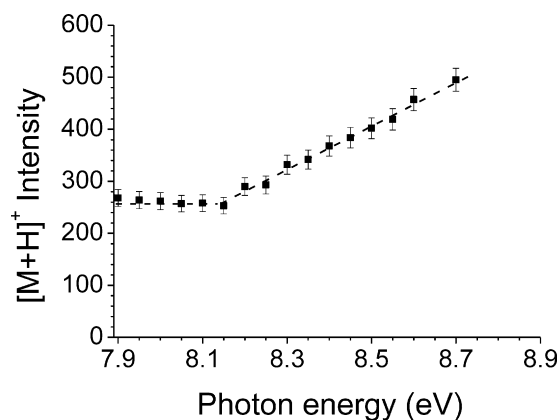


Fig. 2. Ion peak intensity of protonated guanine studied by SR-APPI-MS at 450 °C in H₂O/CH₃OH (50/50, v/v) without dopant as a function of photon energy. Dashed lines are to guide the eye.

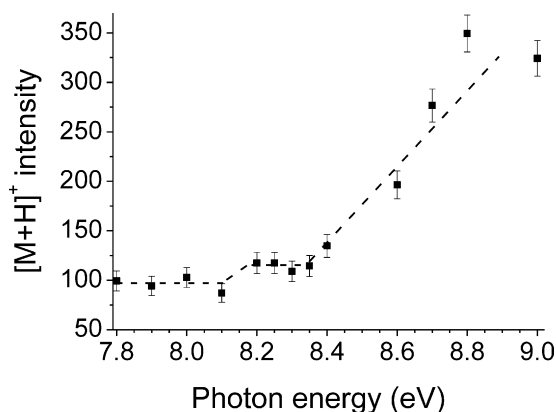


Fig. 3. Ion peak intensity of protonated guanine studied by SR-APPI-MS at 450 °C in H₂O/CH₃OH (50/50, v/v) with anisole as a dopant as a function of photon energy. Dashed lines are to guide the eye.

undergo collisions and react with solvent molecules (reaction (3)). It must be noted that the vertical IE of guanine is 8.1 ± 0.2 eV, in the gas phase [22,23] or in small water clusters [24]. To the contrary, theoretical calculations indicate that in water the vertical ionization of a nucleobase takes place at an energy about 1 eV below that of the gas-phase [25]. The present experimental observations are thus consistent with chemical reactions occurring in the gas phase or in a micro-solvated environment. The enthalpy of the H-atom transfer reaction (3) can be calculated according to the following equation [6]:

$$\Delta_R H = \text{IE}(\text{H}) - \text{IE}(\text{M}) - \text{PA}(\text{M}) + D_{\text{H}}(\text{S}) \quad (7)$$

where IE(H) and IE(M) are the respective ionization energies of the hydrogen atom and of the analyte, PA(M) is the proton affinity of the analyte and $D_{\text{H}}(\text{S})$ is the H-atom bond dissociation energy in the solvent molecule.

Bagag et al. have reported a slightly negative value of $\Delta_R H$ for guanine (M) in methanol (S) (-7.7 kJ mol⁻¹), suggesting the exothermic character of this gas-phase reaction [9]. This explains why no radical cation of guanine is observed in the present experimental conditions. The experimental data are thus in good agreement with the reaction schemes (1)–(3) when no dopant is used.

The same experiments were carried out by adding anisole as a dopant. The corresponding mass spectrum of guanine recorded at 450 °C in water/methanol (50:50, v/v) and with 8.0 eV photons displays two strong ion signals at m/z 152 and m/z 174, as previously described without dopant. Fig. 3 shows the variations of the [M+H]⁺ ion intensity of guanine with a dopant (anisole) as a function of photon energy. The set-up sensitivity (transmission of the UV light through the pumping system, source alignment, etc.) was optimized for each data collection over a one year period. The comparison of the intensity of the absolute [M+H]⁺ signal between Figs. 2 and 3 is not possible. However, the comparison of the relative shape of these two ion yields is possible. For photon energies between 7.8 and 8.1 eV, the intensity of the [M+H]⁺ ion signal does not vary with photon energy, while a minor increase of 20% is observed for photon energies between 8.1 and 8.3 eV, followed by a linear increase for photon energies above 8.3 eV. As seen in Fig. 2, the slope of the linear increase is smaller than that observed in Fig. 3 (slope: 46.0 ± 6.8 counts/eV). Hence, an additional contribution accounts for that increase in Fig. 3. The 8.3 eV value corresponds to the ionization onset of anisole. In order to explain this feature, a mechanism was suggested including the photoionization of the dopant (reaction (4)), followed by a proton transfer from the radical cation of the dopant D^{•+} to the neutral guanine molecules M (reaction (5)) according to their respective PA

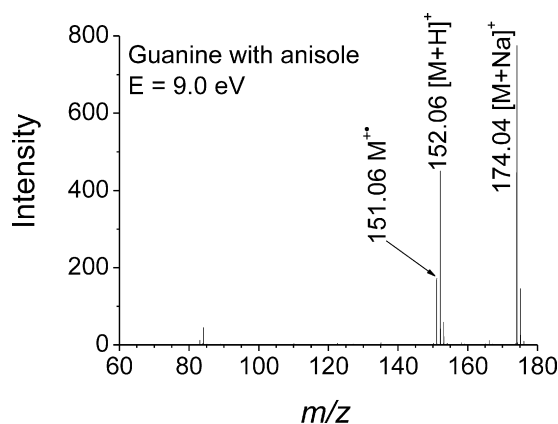


Fig. 4. SR-APPI mass spectrum of guanine recorded at 450 °C in H₂O/CH₃OH (50/50, v/v) with anisole as a dopant and with 9.0 eV energy photons.

(Table 1). This last reaction is directly depending on the amount of radical cation of the dopant D^{••}, which increases when the photon energy increases.

Moreover, for photon energies above 8.15 eV and with anisole, the M^{••} ion is systematically detected (Fig. 4). The intensity ratio of M^{••} over [M+H][•] ions as a function of the photon energy shows a clear increase between 8.2 and 8.7 eV while reaching a quasi-plateau at larger photon energies (Fig. 5). For photon energies larger than the IE value of anisole, i.e. 8.2 eV, photoionization of the dopant becomes effective (reaction (4)), leading to the formation of D^{••} radical cations which can in turn react with guanine by a charge transfer reaction (reaction (6)) according to their respective IE (Table 1). Reactions (5) and (6), which are both exothermic and directly depending on the amount of anisole radical cation formed in the ion source, are thus competitive when the photon energy is larger than the IE value of the dopant. Moreover reaction (6) is entropically favored as no transfer of proton over a tight transition state, like reaction (5), is involved. Reaction (6) will thus be promoted at larger photon energies due to its favorable entropic contribution, explaining the gradual increase of the ratio of the radical over the protonated species. These experimental results are in full agreement with the previously assumed mechanism in which charge exchange and proton transfer could occur in a competitive manner [6,9,13].

By contrast with anisole, toluene (data not shown) acts exclusively in favor of the proton transfer reaction, the molecular ion of guanine being absent in all SR-APPI mass spectra recorded in the same energy range as with anisole. This can be simply explained by

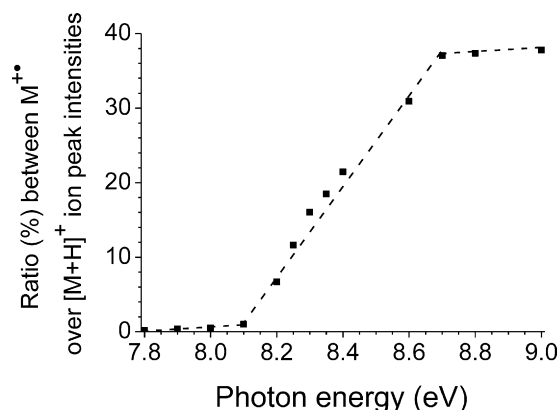


Fig. 5. Ratio (%) between m/z 151 (M^{••}) and m/z 152 ([M+H][•]) ion peak intensities as a function of the photon energy recorded by SR-APPI-MS with anisole used as a dopant. Dashed lines are to guide the eye.

the proton affinity difference between the benzyl radical and the methanol or water clusters [26], indicating that toluene photoions react readily to yield small protonated methanol or water solvent clusters.

4. Conclusion

This work reports the first comprehensive results on the APPI ionization mechanisms obtained with a new set-up: a modified commercial APPI source coupled to a tunable VUV photon source. The relative rates of the competitive chemical reactions which lead to the ionization of guanine, as a function of the photon energy, experimentally confirmed previous assumed mechanisms, thus providing a better understanding of the APPI processes. In the next future, this unique SR-APPI experimental set-up will again implemented to study lipids [27] and peptides [10–12] *in-source* fragmentations and solvent effects [28].

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