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VUV photoionization of gas phase adenine and cytosine: A comparison between oven and aerosol vaporization

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We studied the single photon ionization of gas phase adenine and cytosine by means of vacuum ultraviolet synchrotron radiation coupled to a velocity map imaging electron/ion coincidence spectrometer. Both in-vacuum temperature-controlled oven and aerosol thermodesorption were successfully applied to promote the intact neutral biological species into the gas phase. The photoion yields are consistent with previous measurements. In addition, we deduced the threshold photoelectron spectra and the slow photoelectron spectra for both species, where the close to zero kinetic energy photoelectrons and the corresponding photoions are measured in coincidence. The photoionization close and above the ionization energies are found to occur mainly via direct processes. Both vaporization techniques lead to similar electronic spectra for the two molecules, which consist of broadbands due to the complex electronic structure of the cationic species and to the possible contribution of several neutral tautomers for cytosine prior to ionization. Accurate ionization energies are measured for adenine and cytosine at, respectively, 8.267 ± 0.005 eV and 8.66 ± 0.01 eV, and we deduce precise thermochemical data for the adenine radical cation. Finally, we performed an evaluation and a comparison of the two vaporization techniques addressing the following criteria: measurement precision, thermal fragmentation, sensitivity, and sample consumption. The aerosol thermodesorption technique appears as a promising alternative to vaporize large thermolabile biological compounds, where extended thermal decomposition or low sensitivity could be encountered when using a simple oven vaporization technique. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793734]

I. INTRODUCTION

The study of large biomolecules, such as DNA or proteins, requires prior and extensive knowledge of the physicochemical properties of their small building blocks, i.e., nucleobases and amino acids. In particular, the investigation of ionized species of DNA or RNA has gained importance during the last decades, because the damage produced by the interaction between ionizing radiation and biological matter leads to hazardous genetic mutations with enhanced risk for cancer.[1–3] The mechanisms underlying DNA or RNA lesions are still under study and require the precise determination of thermochemical properties such as the ionization energy (IE) of the reactive species, their spectroscopy, their nuclear dynamics, and a comprehensive understanding of their electronic structure.

The ionization of nucleobases and related compounds has been widely studied since the 1970s because of their biological importance. Ultraviolet photoelectron spectra have been recorded by several groups, often related to theoretical works.[4–12] Photoionization mass spectrometry (PIMS) works are reported in Refs. 13–15, while electron impact mass spectrometry studies are detailed in Refs. 16 and 17. Theoretically, dedicated investigations were performed in order to predict the adiabatic ionization energies (AIE) or vertical ionization energies (VIE), and/or to assign the bands observed in the photoelectron spectra, i.e., their π or n character, for example.[18–26] Moreover, combined experimental and theoretical studies on ionization properties of dimers of nucleobases have been reported too.[27–30] These dimers represent models of the non-covalent interactions occurring during the DNA double strand formation or in the RNA folding.

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Considering this extensive amount of literature, nucleobases can be contemplated as good models for a technical comparison between different vaporization techniques of biomolecules. Nowadays, photoelectron-photoion coincidence (PEPICO) and Threshold Photoelectron Photoion Coincidence (TPEPICO) experiments using tunable vacuum ultraviolet synchrotron radiation (VUV-SR) offer accurate determinations of IE values. The main difficulty in such experiments is the way to generate jet-cooled *neutral* biomolecules inside the ionization chamber. These (T)PEPICO experiments typically use an in-vacuum temperature-controlled oven, which is installed inside the molecular beam chamber. Such a setup is able to generate a molecular vapor that is mixed with a carrier gas (He, Ar, N_2) and expanded through a micrometric nozzle/skimmer assembly before crossing the VUV-SR photon beam. Therefore, this technique requires volatile and thermally stable molecules. Nevertheless, biomolecules such as DNA bases or peptides do not in general fulfill these conditions. The quality of the spectra depends on the detection sensitivity of the instrument, which ultimately fixes the temperature needed to produce a sufficient mixing ratio of the compound inside the molecular beam.

Pulsed laser desorption has also been employed for the production of neutral biomolecules in the gas phase.[15,31,32] The low repetition rate and the poor pulse-to-pulse stability of the laser made difficult to easily couple this technique with a continuous ionization source such as synchrotron radiation. In addition, laser desorption apparently produces a large tautomer and/or conformer distribution as has been demonstrated by combined experimental and theoretical work presented in Refs. 31 and 33 for guanine and cytosine, even when the laser-desorbed molecules are picked up by a molecular rare gas jet right behind the nozzle.

More recently, aerosol sources have been developed in order to propagate fragile molecules efficiently to the gas phase. Generally, these sources make use of a thermal desorption step when aerosol particles of nanometric size, consisting of the pure substance under study, impinge on a heater. In 2006, the group at the Chemical Dynamics beamline at the Advanced Light Source coupled successfully such a source to a VUV-SR mass spectrometry (MS) photoionization apparatus.[34–36] They determined, for instance, adiabatic ionization energies of organic molecules, amino acids, small peptides, or β-carotene. Very recently, Gaie-Levrel *et al.*[37] combined a thermal desorption aerosol setup with a Velocity Map Imaging (VMI) electron analyzer which is operated in coincidence with a Wiley-McLaren ion time of flight (TOF) mass spectrometer and using VUV-SR as a single photon ionization source. This unique apparatus allowed measuring accurate AIEs and fragment appearance energies (AEs) from a state-selected parent ion. Afterwards, a detailed analysis of the ion electronic structure and of its state-to-state unimolecular fragmentation dynamics is deduced. In this way, AIEs of tryptophan and phenylalanine molecules and AEs of major fragments were measured with high accuracy. A small quantity of sample (few tens of milligrams for ~24 h experiment) was used.

In this work, we present for the first time close to zero kinetic energy photoelectron spectra in coincidence with their corresponding photoions on two natural nucleobases, adenine and cytosine, brought in the gas phase by using both aerosol thermal desorption and oven vaporization. These molecules represent the purine and pyrimidine class, respectively. The two vaporization techniques are implemented on the same ionization chamber and within the same PEPICO spectrometer, i.e., the same ion/electron detectors. As far as we know, it is the first time that two different vaporization techniques, implemented on the same apparatus, are directly compared with respect to their performances for the analysis of polar and thermolabile biomolecules. We will show that the aerosol technique can be considered as a soft technique for getting into the gas phase biomolecules, especially the fragile ones. Concerning adenine and cytosine photoionization, the addition of the electron kinetic energy adds a new dimension that leads to a much better definition of the electronic structure of the cation, and grants access to its state-selected photochemistry. For both molecular species, photoionization is viewed to occur mainly via direct processes close and above the IEs. The photoelectron spectra consist mainly of large structureless bands because of either the complex electronic structure of the cations or participation of various tautomers or both. In the past, such assumptions were emitted by several groups but never definitely established. Finally, accurate thermochemical data for adenine are deduced from the spectra.

II. EXPERIMENTAL DETAILS

The monochromatised VUV ionizing radiation was delivered by the DESIRS beamline,[38] at the 3rd generation, French synchrotron facility SOLEIL located at St Aubin, France. For these experiments, the DESIRS 6.65 m normal incidence monochromator was operated at a typical photon bandwidth of about 2.5 meV. The harmonics other than the fundamental were absorbed by a gas filter standing upstream the beamline,[39] which was filled with 0.17 mbar of Kr. Rare gas lines were used to calibrate the energy scale of the spectra leading to a precision of $\pm$ 5 meV.

Adenine and cytosine were purchased from Sigma Aldrich (Saint-Quentin Fallavier, France). For oven experiments, the sample (~1 g) was directly deposited as a powder in the in-vacuum temperature-controlled oven installed inside the SAPHIRS molecular beam chamber. The temperature was set at 540 K for adenine and 545 K for cytosine. The generated vapor was mixed with 1 bar of He to avoid DNA basis clustering and then expanded through a 50 μm nozzle into a first expansion chamber maintained at 10^{-4} mbar. The jet-cooled molecular beam (~ at 80 K) was then introduced into the ionization chamber through a 1 mm skimmer before interacting with the VUV-SR photon beam in the DELICIOUS II spectrometer described in detail in Ref. 40. Briefly, DELICIOUS II detects photoelectrons with a VMI analyzer, capable of recording threshold photoelectrons with sub-meV resolution, or fast electrons (up to 17 eV kinetic energy) with a 5% energy resolution. In the opposite direction, ions are detected in coincidence by a Wiley-McLaren TOF mass spectrometer, whose mass resolution is about 130. TPEPICO spectra were treated in a way such that the threshold electron resolution obtained is 40 meV for adenine and 80 meV for cytosine.

For aerosol experiments, samples were dissolved in water to yield a concentration of 1 $g\,l^{-1}$. The solution was nebulized by gaseous nitrogen using a constant output atomizer (TSI model 3076) followed by a diffusion dryer (TSI model 3062) where water is carried away yielding solid nanoparticles of the pure compound. Downstream, the aerosols entered the SAPHIRS expansion chamber via an aerodynamic lens system that focuses the particles into a narrow beam of submm size (see Ref. 37 for details). Inside the interaction region at the center of DELICOUS II, the nanoparticles were thermally vaporized using a thermal desorption module inserted opposite to the particle propagation direction. The temperature of the thermal desorption system was set at 423 K.

In both cases, TPEPICO spectra were recorded by considering the sum signal of mass-selected photoelectrons having kinetic energies close to zero vs. the photon energy. The mass selection ensures that only the photoelectrons associated with a specific ion are detected in coincidence. These spectra have been normalized to the photon flux by using a VUV Si Photodiode (IRD, AXUV100).

III. RESULTS AND DISCUSSION

We display in Figure 1 the integrated TOF spectra of adenine and cytosine over the scan energy range. The DNA bases were vaporized using in-vacuum temperature-controlled oven vaporization and aerosol thermal desorption. When using the aerosol source, the TOF spectra are composed of two peaks: one at *m/z* 28 corresponding to N_2 (due to the remaining second order radiation ionization of carrier N_2) and a second one corresponding to the DNA basis parent ion. When using the oven, several other peaks in addition to the DNA basis peaks appear in the TOF spectra. In the case of adenine, only a mass around *m/z* 94 can be observed, with an AE below 8 eV. This mass could come from an impurity in the oven or the ionization chamber, or be the product of thermal decomposition of either adenine or its polymers. In the case of cytosine, several masses lighter than the parent appear in the TOF, such as *m/z* 17 (assigned to NH_3 by its TPEPICO curve), *m/z* 68 (AE_{68} = 8.76 eV), and *m/z* 94 (AE_{94} < 8 eV). Presently, it is hard to give a definite statement to explain the origin of these features. Again, the latter two could be assigned to impurities of thermal decomposition. Anyway, these additional peaks are without any consequences on our treatment of the DNA bases since they can be totally filtered out in the adopted coincidence scheme. Nevertheless, it shows that previous works with oven vaporization, where coincidences between ions and electrons were not performed, may contain additional structures wrongly assigned to DNA bases.

We present in Figs. 2 and 3 the TPEPICO spectra of adenine and of cytosine from threshold up to few eVs above, i.e., in the spectral region covering their ionization potentials and those of their lowest electronic excited states. The 2D spectra of the parent ions for photoelectrons having kinetic energies from 0 to 190 meV are shown in Figures S1 and S2 of the supplementary material[41] when using oven. They were obtained by plotting the photoelectron spectra as a function of the photon energy.[42–44] These 2D matrices reveal that the single photoionization of adenine and of cytosine occurs mainly by a direct process in the energy ranges of interest, so that autoionization processes can be neglected. Eventually, these matrices can be used directly to perform a slow photoelectron spectra (SPES) treatment.[42–44] The corresponding spectra are displayed in Ref. 41 and they resemble the TPEPICO spectra. Here, we will present and discuss only the TPEPICO

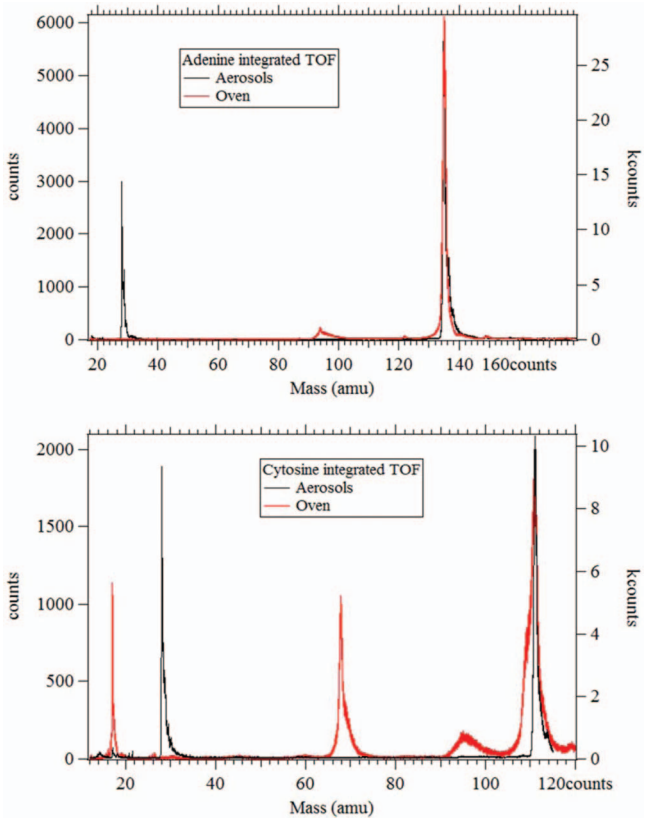

FIG. 1. Integrated TOF spectra of adenine (top panel) and cytosine (bottom panel) over the scan energy range. The DNA basis were vaporized using in-vacuum temperature-controlled oven vaporization (red line and left y-axis) and aerosol thermal desorption (black line and right y-axis). The intense peak at 28 amu in the aerosol spectrum corresponds to the N_2 used as carrier gas. Other differences between the spectra are due to impurities in the oven.

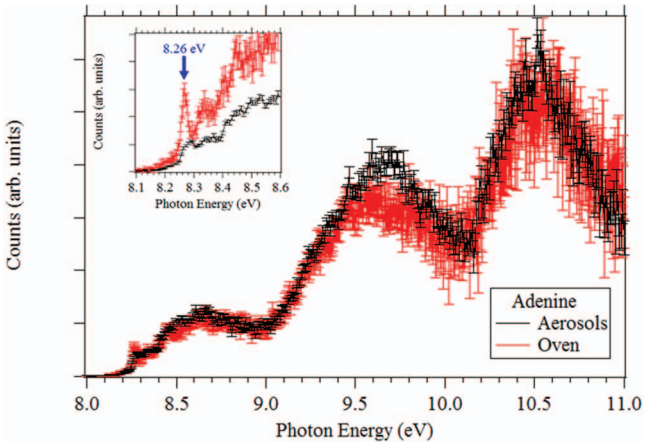

FIG. 2. TPEPICO spectra of the adenine parent obtained with 40 meV threshold electron resolution. The black curve is when adenine is vaporized with the aerosol source and the red curve is for in-vacuum oven. The inset presents an energy close up of the threshold region.

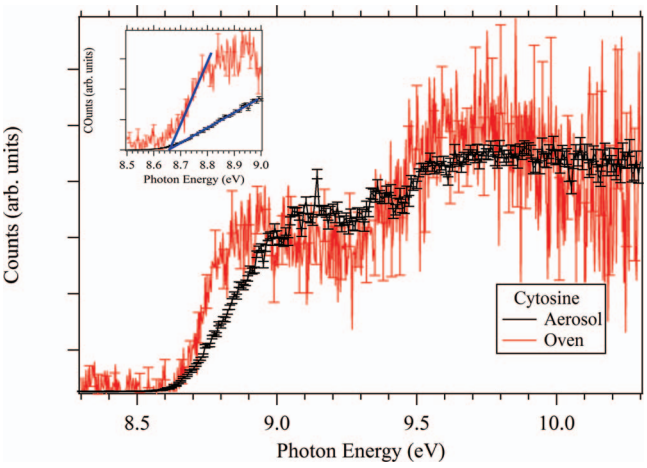

FIG. 3. TPEPICO spectra of the cytosine parent obtained with 40 meV threshold electron resolution when using the aerosol source (black curve) and with 80 meV (red curve) when using the in-vacuum oven. The inset is an enlargement for the threshold ionization energy where the oblique lines are to enlighten the slopes at the ionization threshold. See text.

analysis since the SPES one is not possible with the aerosol experiment because of the distortion on the photoelectron images when using the thermodesorption technique. Therefore, the TPEPICO spectra are performed using 40 meV or 80 meV threshold kinetic energies which are relatively wide compared to our photon resolution (2.5 meV). Note that, particularly in the case of adenine, the thermochemical properties are deduced with a small precision (±0.005 eV), which is directly related to the presence of an adiabatic peak. This is solely possible through the use of electron/ion coincidences, and would not appear in the simple total ion yield, further highlighting the interest of the methodology used here.

A. Assignment of the adenine TPEPICO spectra

Recent theoretical systematic works on the tautomers of neutral adenine show that the most stable tautomer is the 9H-adenine followed by two other tautomers, i.e., 3H-adenine and 7H-adenine at energies of 29 and 31 kJ mol^{-1} with respect to 9H-adenine.[26,45–48] Plützer *et al.*[49] performed IR-UV and R2PI double resonance spectroscopy of adenine, vaporized in an oven before expansion through the nozzle. The bands observed in their jet-cooled UV and IR adenine spectra (36 050–36 700 and 3200–3700 cm^{-1}, respectively) are attributed to a unique tautomer, the 9H-adenine. These findings are confirmed also by MP2 and density functional theory calculations. These authors stated in their conclusion that without jet-cooling, the IR spectrum is more complex most likely because of the presence of other tautomers. One year later, Nir *et al.*[31] demonstrated that gas-phase adenine produced by heating and then followed by jet-cooling may lead to the presence of two distinct isomers. In contrast, Bravaya *et al.*[26] proved recently that jet-cooling of the adenine vaporized sample leads efficiently to the predominance of the most stable tautomer prior to ionization. When using oven for producing gas phase adenine, we do expect that our TPEPICO spectrum results from the single photon ionization of 9H-adenine as in the work of Bravaya *et al.*[26]

Below 8 eV, the TPEPICO spectra of adenine show no signal. The signals start increasing above hν = 8 eV, which is consistent with previous experimental studies.[8–10] For hν ≤ 11 eV, a major ion signal at *m/z* 135 was detected, corresponding to the radical cation $M^{\bullet+}$ of adenine and no fragment ions were observed (see Ref. 41). This is in perfect agreement with the data obtained by Jochims *et al.*[14] where AEs of fragments, determined at BESSY synchrotron facilities (Berlin-Adlershof), are well above 11 eV.

The TPEPICO spectrum is composed of three large bands centered at 8.6, 9.6, and 10.5 eV, respectively. These bands are structureless and have been already described in previous HeI and SR based PES.[8–10] Based on the high level computations by Krylov and co-workers,[26] i.e., equation-of-motion coupled-cluster model with single and double substitutions for ionized systems (EOM-IP-CCSD), the first band corresponds to the ionization of the π-type HOMO. The second and third bands are derived from ionization from π- and σ-like molecular orbitals. They all correspond to Koopmans-like ionization processes.[26] The computed IEs for 9H-adenine states were defined as follows: π_1 (8.37 eV), n_1 (9.37 eV), π_2 (9.60 eV), n_2 (10.42 eV), π_3 (10.58 eV), which compare well to the maxima of the bands of our spectrum. In addition, Nir *et al.*[31] determined an accurate vertical ionization energy of 9H-adenine (VIE = 8.606 ± 0.006 eV), which is in excellent agreement with the maximum of our first band, whereas HeI PES experiments reported VIEs slightly lower (8.44 ± 0.03[4] and 8.48 eV[8]). The IE values determined by electron impact are widely distributed over a 1 eV range,[50–52] which make any comparison quite hard to perform. Nevertheless, the close agreements between the most resolved previous experimental determinations and our experimental spectrum confirm the contribution of a single tautomer, i.e., 9H-adenine.

A significant difference between the present oven jet-cooled and the aerosol TPEPICO spectra occurs close to the threshold ionization energy region of adenine. For illustration, we depict in the inset of Figure 2 an energy closeup of the first ionization threshold of adenine, where the oven jet-cooled spectrum shows a clear sharp peak at IE corresponding to the $\tilde{X}0_0^0$ photoionization transition of 9H-adenine. The oven SPES spectrum of adenine[41] presents also such a sharp peak. This allows determining accurately the adiabatic IE of 9H-adenine as AIE = 8.267 ± 0.005 eV, which is in excellent agreement with previous ones obtained by PIMS consisting in simply measuring the relative intensity of the parent ion versus the photon energy (8.26 eV;[13] 8.20 ± 0.03 eV[14]). In contrast, the aerosol spectrum shows a much less marked adiabatic transition, consistent with a higher neutral temperature leading to a smearing of the ionization edge because of the likely contribution of vibrational hot bands in the neutral. In addition, the relative intensities of the TPEPICO bands exhibit a slight dependence on the vaporization process, with the maximum of the second band also showing a slight energy shift.

When we compare the VIE and the AIE of 9H-adenine, we find ~0.34 eV. This difference is consistent with theoretical estimations of the deviation between AIE and VIE using *ab initio* calculations.[26,53–56] These theoretical studies showed that ionized adenine did not lose its planarity, meaning that the

Franck-Condon transition shift is only caused by bond length and angle modifications between the neutral ground state and the radical cation of adenine leading to a relatively small difference between AIE and VIE for 9H-adenine.

The heat of formation of the adenine radical cation $\Delta_f H^{298}$(adenine cation) can be estimated using the heat of formation of neutral adenine ($\Delta_f H^{298}$(adenine) = 207 ± 8 kJ mol^{-1}[57]) and our measured value of AIE = (797.0 ± 4.8) kJ mol^{-1} leading to a final value of $\Delta_f H^{298}$(adenine cation) = 1004 ± 9 kJ mol^{-1}. This result is significantly greater than the value given by Lias *et al*. (960 kJ mol^{-1}) (see Ref. 57 for more details). The latter is based on an earlier IE value of 7.8 eV, which is probably too low. Our value is in better agreement with the one given by Jochims *et al*.[14] ($\Delta_f H^{298}$(adenine cation) = 998 ± 11 kJ mol^{-1}) and by Hwang *et al*.[58] ($\Delta_f H^{298}$(adenine cation) = 1029 ± 13 kJ mol^{-1}). The latter authors used a dual cell Fourier transform ion cyclotron resonance mass spectrometry for their measurements.

B. Assignment of the cytosine TPEPICO spectra

Extensive *ab initio* calculations on the energetics of six tautomers of cytosine and their ionization energies have been performed (see Refs. 26, 28, and 59 for the most recent ones). In contrast to adenine, the tautomers of cytosine are much close in energy, where five different tautomers are within energy differences lower than 11.5 kJ mol^{-1}. Hence, probably a mixture in the gas phase prevails in both oven and aerosol experiments. Experimentally, photoionization mass spectra of cytosine have been recorded recently by Plekan *et al*.[60] with rare gas lamps at five different VUV excitation energies. The group at the Advanced Light Source[28,61] and Trofimov *et al*.[10] used VUV-SR to measure the differentiated photoionization efficiency (PIE) curves to obtain the PES spectrum of cytosine. In these works, cytosine was produced by oven vaporization. They showed the co-existence of several tautomers of cytosine prior to ionization even after jet-cooling, and that the composition of the neutral gas is strongly dependant on the technique used for vaporization. Thus, Trofimov *et al*.[10] assigned the PES of cytosine by assuming the existence solely of the lowest tautomer of cytosine, C2b, while the group at the Advanced Light Source was suggesting the contribution of all five lowest tautomers of cytosine to their spectra.[28] This makes the situation more complicated for cytosine than for adenine and hence worth to investigate using different vaporization techniques (i.e., different gas temperatures) as in the present work.

The TPEPICO spectra of cytosine shown in Figure 3 start by a sharp increase of the signal close to the IE of cytosine. Then, the spectra are composed of several overlapped bands corresponding to the population of the ground and the two first excited states of this cation. We deduce the AIE of cytosine to be 8.66 ± 0.01 eV by linear extrapolation of the first onset, since there is no clear adiabatic transition in the spectra. Our experimental value of AIE is in very good agreement with the latest experimental value reported by Kostko *et al*.[28] (8.60 eV), which is deduced from a differentiated PIE curves. Previous experiments based on electron impact ionization (9.0 ± 0.1 eV and 8.9 ± 0.2 eV[62]), PIMS (8.65 ± 0.05 eV[62]), and PES (8.94 ± 0.03 eV and 8.45 eV[4,10,63,64]) indicate a significant discrepancy in the values. This can be partially explained by different compositions of the cytosine tautomer distribution in the gas jet prior to photoionization.

Our experimental spectra, especially the one obtained after oven vaporization, approach nicely the one computed by Bravaya *et al*. (cf. Figures 11 and 12 of Ref. 26). Moreover, the core-level PES study[65] of cytosine and the free energy calculations[66,67] suggested that three tautomers of cytosine are populated upon thermal vaporization at 450 K, with a dominant contribution of tautomers C2a and C2b (of ∼60%). Accordingly, we believe that several tautomers give non-vanishing contribution to our spectra at different extents depending on the temperature (see below). Because of similarities between our spectra and the theoretical ones by Bravaya *et al*.,[26] we expect that at least five tautomers (for instance, C1, C2a, C2b, C3a, and C3b) contribute. For the assignment of the bands, we refer to the detailed discussion undertaken by Krylov and co-workers[26,28] for that purpose.

C. Insights into the electronic structure of adenine$^+$ and cytosine$^+$ cations

Recently, we treated the VUV photoionization of 2-pyridone and its tautomer, of δ-valerolactam, and of 3-hydroxyisoquinoline.[42,43,68,69] These molecules are considered as DNA basis analogues, and their dimers are used as models for the DNA basis pairing. We recorded the slow photoelectron spectra obtained after VUV photoionization under the same experimental conditions as presently when using oven vaporization followed by jet-cooling. In these previous works, the achieved experimental total resolution was 9–10 meV. The recorded spectra consist of well-resolved rich vibrational structure, which were assigned to the population of the vibrational bands of the cationic forms in their ground and electronically excited states. Therefore, the actual experimental resolution should allow the resolving of the vibronic structure of the adenine$^+$ and cytosine$^+$ cations. Nevertheless, the spectra of Figs. 2 and 3 are structureless, most likely due to orbital congestion. This may be related to the intrinsic structure of adenine and cytosine neutrals and ionized species. For explanation, several arguments may be invoked: (i) unfavorable Franck-Condon factors upon photoionization of adenine and cytosine; (ii) possible contribution of several isoenergetic tautomers, as for cytosine; (iii) strong vibronic couplings between the lower doublet electronic states of the DNA bases cation (adenine$^+$ or cytosine$^+$) since these electronic states are lying closely. These facts were already suggested previously.[26,28] Our experimental study confirms these assumptions since improving the electron resolution does not help to better characterize the vibronic structure of adenine$^+$ and cytosine$^+$. Surely, the electronic structure of DNA bases is more complicated than the biomimetic molecular systems used as models. The origins of such complexity are still under investigation.

D. Vaporization of DNA bases: Comparative study

The main advantage of the in-vacuum temperature-controlled oven resides in the subsequent adiabatic expansion,

which cools down and effectively narrows the Boltzmann distribution of neutral populations. Indeed, the TPEPICO spectrum for adenine is well assigned based on the predominance of one tautomer in the jet-cooled molecular beam. This is also in good agreement with the main conclusions of the computational and PIE studies performed by Bravaya *et al.*[26] and the earlier experiments by Plützer *et al.*[49] In contrast, the aerosol thermodesorption technique transfers a certain amount of internal energy to the neutral, which at worst can correspond to the thermodesorber's temperature. In the case of adenine, the tautomers are spaced enough so that the 423 K on the thermodesorber tip corresponds to not enough thermal energy to surmount the tautomerization barrier, and only the 9H-adenine is present. It is interesting to note that, for both cytosine and adenine, this temperature is around 393 K, which is colder than the one needed for oven vaporization. This rather low temperature presents an advantage with respect to other vaporization methods such as laser desorption, where the high power density needed (about 10^6 W cm^{-2} at least) conveys a relatively high amount of internal energy to the molecule.[15,31,32]

Although the TPEPICO spectra shown in Figs. 2 and 3 have similar shapes for both oven and aerosol vaporization, there exist small differences due to the different neutral internal energies that are worth noting. First, the relative intensities of the bands when using either oven or aerosols are not exactly equal. Second, the slopes of the TPEPICO onsets are more pronounced when using oven vaporization, as can be clearly seen, for instance, in the first cytosine onset starting at 8.6 eV (see Figure 3). Based on the interpretation given above, at least five tautomers can contribute to the spectra, the slope difference should arise mainly from a variation of the tautomer population,[10] with ionization onsets spread in the 8.6–8.8 eV range,[28] combined to a likely contribution from the Boltzmann vibrational population. Third, the vibronic bands are more resolved using oven vaporization, and this is clearly the case in the first onset of the adenine TPEPICO spectra, where the oven spectrum shows a well-resolved peak for the $\tilde{X}0_0^0$ band. Besides the neutral temperature, another issue that could compromise the resolution in the aerosol experiments, is its detrimental effect on the shape of the extraction field,[37] which is critical to the ultimate resolution attained by the velocity map imaging analyzer, and which could be at the origin of the less marked onset of adenine around 8.26 eV. However, the presence of the thermodesorber would not affect the total ion efficiency curves, and we still observed a difference in the onset slope in the PIE between both methods, so that the lower resolution found in aerosol thermodesorption can be mainly attributed to the higher neutral internal energy.

Another interesting difference between the oven and aerosol thermodesorption techniques clearly visible on the TPEPICO spectra is that, in this particular case, the latter provides a much better signal/noise (S/N) most likely because of the reduced contribution of false coincidences originating from molecules other than the DNA basis. This could already be seen on the integrated TOF where the oven use leads to a $\sim$ 5-fold lower signal on the parent peak as compared to the aerosol thermodesorption case (see Figure 1). Of course, one can argue that the oven temperature could be increased to augment the S/N ratio, but this would be achieved at the expense of resolution (due to a higher temperature of the expansion), and at the risk of thermal decomposition. It is nevertheless surprising that a higher S/N ratio is obtained for the aerosols when considering that the thermodesorber temperature of vaporization is at least 120 K colder. This can be explained by the high conversion efficiency of thermodesorption of the aerosol by the hot finger providing a localized plume of intact parent neutral molecules in the interaction region to be probed by the VUV photon beam. In the case of the molecular beam associated with the oven technique, most of the sublimated molecules finish into the pumping system of the jet chamber, the skimmer transmitting only $\sim$1% of the molecules present in the jet. This is clearly related to the product consumption issue, which is another important consideration when designing an experiment. Indeed, we estimate that only 50 mg of the compound were consumed over the $\sim$8 h that took acquiring the TPEPICO spectra with the thermodesorption technique, while oven experiments needed at least 1 g for the same experiment, i.e., 20 times more for a worse signal-to-noise ratio. The use of aerosols is, therefore, promising for the studies of costly samples such as drugs or pure enantiomeric organic compounds which can, in some cases, largely compensate the higher neutral temperature of the produced gas phase molecules.

IV. CONCLUSIONS AND PERSPECTIVES

We have recorded the threshold electron spectra of adenine and cytosine parents by combining VUV synchrotron radiation and electron/ion coincidence techniques. The results have been used as a diagnostic to present a detailed comparison between an in-vacuum temperature-controlled oven and an aerosol setup coupled to a thermodesorber module, for the production of the intact neutral molecular species. In this particular case, we demonstrate that aerosol thermodesorption offers a lower sample consumption while still providing a satisfactory sensitivity, but at the expense of imparting a higher internal energy to the neutral molecules and in our case, results on relatively limited overall experimental resolution. Note that an improvement of the thermodesober should be able to get rid from this disadvantage. However, we believe that, due to the low working temperature, aerosol thermodesorption is a competitive alternative to laser desorption for the production of large neutral biomolecules, such as nucleotides, oligopeptides, or polysaccharides, especially for thermolabile compounds. In the near future, we expect to be able to increase the electron energy and ion mass resolution for aerosol thermodesorption experiments by decreasing the diameter of the thermodesorber tip. In addition, the aerosol setup needs to be miniaturized in order to substantially decrease the sample consumption at few mg for a complete PES. The next limitation concerns the cost and the availability of the biological samples. Combined with UV photofragmentation spectroscopy on ions stored in ion trap mass spectrometer,[70,71] both techniques will allow us better understanding on the biological processes implying radical formation following UV photon absorption on neutral and charged species.

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