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VUV photophysics and dissociative photoionization of pyrimidine, purine, imidazole and benzimidazole in the 7–18 eV photon energy range

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ABSTRACT

Photoionization mass spectrometry is used to study ionization processes and fragmentation pathways of four prebiotic species, pyrimidine, purine, imidazole and benzimidazole, in the 7–18 eV photon energy region, with synchrotron radiation as excitation source. These molecules are possible precursors of the nucleic acid bases that occur in DNA and RNA. Ionization energies and ion appearance energies are reported. They are compared with electron impact and other studies and are discussed in terms of the electronic and nuclear structures of these species and their cations. The ion appearance energies, in conjunction with thermochemical data, were used to propose dissociative photoionization pathways, principally involving loss of HCN molecules in each of the four species. Astrophysical implications of the results concern the prospects for observation and survival of these molecules in the interstellar medium, in comets and in meteorites. Suggestions are made concerning suitable sites for radioastronomical searches for these purines and pyrimidines.

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1. Introduction

The vacuum ultraviolet (VUV) photophysical and photochemical properties of pyrimidine, purine, imidazole, and benzimidazole require study, in particular because of the possible delivery of these molecules from space to the early Earth, as well as the role that they could have played in the origin and development of life on earth, and perhaps on other planets or satellites [1–4]. Purine is a molecular skeletal building block of the nucleic acid bases adenine and guanine, while cytosine, thymine and uracil are related to pyrimidine. The imidazole structure is found in purines, while benzimidazole is a close relative of purine. We have recently studied the VUV photophysics of three nucleobases (adenine, thymine and uracil) [5] and seek here to investigate their possible prebiotic precursors.

The gas phase mid-UV photochemistry of purine nucleic acid bases has been explored recently by resonant two photon ionization spectroscopy [6–9]. Condensed-phase UV spectra of pyrimidines and purines have been measured earlier and have been reviewed by Callis [10]. For nucleobases, upon excitation in the 280–300 nm region, where they absorb strongly [11,12], the most prominent photophysical feature in the gas phase, in this spectral region, is that of internal conversion. This very fast relaxation process, on the ps time-scale, protects the nucleobases from UV induced fragmentation [10,13,14], thus providing a possible reason why evolution has arrived at these particular building blocks for the storage of genetic information [15].

In the VUV ($E_{photon} \sim 7$–20 eV), the photoabsorption cross section of the DNA and RNA nucleobases is higher than in the UV [12,16–18], similar to the case of polycyclic aromatic molecules and related compounds [19] and this is no doubt also the case for the molecules under study here, but which has been verified only for pyrimidine [20]. Apart from photoelectron spectral studies [21–24] and some early mass spectrometry work [25–28] there has been relatively little previous investigation of ionization phenomena of the molecules under study here. Except for the work on imidazole of Main-Bobo et al. [28], no dissociative photoionization studies have been reported. Furthermore, few adiabatic IEs have been reported and these are uncertain [29,30]. In this paper, we report results from a photoionization mass spectrometry (PIMS) study of pyrimidine and purine, and of the chemically related molecules imidazole and benzimidazole. Besides their astrobiological interest, we note that the imidazole ring can accept a hydrogen bond from the exocyclic amine of guanine [31], and that benzimidazole is known to be an important structural component in drug design [32], in particular it is an essential part of many antineoplastic derivatives [33]. Histidine, which is an amino acid involved

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in the active sites of proteins, contains the imidazole nucleus, so that the latter plays an important role in living entities.

We have measured the photoion yield curves of parent and fragment ions as a function of incident photon energy between 7 and 18 eV and report adiabatic ionization energies (IE) and fragment appearance energies (AE) that were previously unknown or poorly known. The limited data previously available, mainly from electron impact measurements suffer from insufficient precision. More extensive AE data for these compounds is important in order to explore their VUV degradation pathways. In particular, this information permits assessment, on thermochemical grounds, of possible ionic and neutral products, as well as enabling one to choose between alternative dissociation processes. A preliminary account of some aspects of this work has been reported elsewhere [34].

2. Experimental

Synchrotron radiation from the Berlin electron storage ring BESSY II was monochromatised by a 3 m normal incidence monochromator, and then focussed into a differentially pumped gas cell which can be heated up to 400 °C but was here restricted to lower temperatures. The experimental set-up is described in more detail elsewhere [35]. Vapours were introduced into the ionization chamber by direct evaporation of liquid or solid samples in open containers placed 1–2 cm below the position of the incident VUV radiation within the ion extraction zone. The temperature, typically between 100 and 130 °C, was kept as low as possible in order to avoid thermal degradation of the compounds. When some thermally induced dissociation did occur this was easily identified by the observed mass spectra, thus enabling us to modify experimental parameters so as to achieve suitable experimental conditions of minimal thermal dissociation and satisfying signal intensity. In cases where water impurity was observed in the mass spectra this generally resulted from residues of cleaning procedures of the apparatus carried out between experimental runs.

Parent and fragment ions formed by photoionization were measured using a quadrupole mass spectrometer (Leybold Q200) (which tends to discriminate against higher mass ions, especially at high mass resolution), and ion yield curves were obtained through photon energy scans with measuring intervals of 10 meV. The yield curves of the principal ions observed are normalized to the incident photon flux measured by detecting the fluorescence of a sodium salicylate coated window. Wavelength dependent photon flux changes are due to the grating transmission function and decreasing electron storage ring current. The yield curves are presented in appropriate figures. Spectral bandwidth

of the incident monochromatic radiation was typically 0.2 nm. Ionization energy determinations were carried out with a MgF$_2$ filter (100% cut-off effective at 11 eV) in order to suppress stray light and second-order radiation. Ion appearance energies were determined mainly with the aid of semi-log plots of the ion yield curves (see below). Appearance energies above 16 eV could not be measured for the weaker fragment ions because of diminished grating reflectivity in this spectral region. The samples were commercial products (Sigma–Aldrich) of best available purity. Their formulae are given in Fig. 1.

3. Results and discussion

The appearance energies measured for the ions correspond to *effective* thermochemical energy values. They are a function of instrumental detection sensitivity and also reflect effects of thermal energy since any activation barrier of a particular fragmentation process (Eq. (1)) could lead to depositing internal or kinetic excess energy in the fragments. We note that the kinetic energy shift has two main factors: limited detection sensitivity and the thermal energy stored in the parent neutral. With respect to the true 0 K AEs, their effects displace the measured AEs in opposite directions. It has been pointed out by Chupka [36] that these two effects tend to cancel out each other, yielding *in fine* reasonably accurate AEs. Therefore, we did not "correct" our AEs for any effect but just give them as they are read from the semi-log ion yield curves by fitting straight lines to the noise and to the ion signal rise in the threshold region. The photon energy at the intersection of these two lines is assigned to the measured AE value. Applying different fits, the precision is estimated by visual inspection of the variation of the intersection. It is thus critically dependent on the sharpness of the ion signal rise in threshold region.

The measured AE's are used to calculate *apparent* enthalpies of formation of fragment ions m_1^+ ("app-$\Delta_f H$") for different possible fragmentation pathways, using Eq. (2)

$$M + h\nu \rightarrow M^+ + e^- \rightarrow m_1^+ + m_i \tag{1}$$

$$AE + \Delta_f H_{gas}(M) - \sum[\Delta_f H_{gas}(m_i)] = app - \Delta_f H_{gas}(m_1^+) \tag{2}$$

The apparent $\Delta_f H(m_1^+)$ values are then compared to tabulated standard thermochemical enthalpies of formation $\Delta_f H(m_1^+)$, thus permitting assignment of particular fragmentation channels. If literature $\Delta_f H(m_1^+)$ values are not available, the app-$\Delta_f H°$ values represent new, upper limit, values. We hope, as a result of our measurements, to incite theoretical work on the thermochemistry of these fragments (neutral and cationic) in order to further clarify the fragmentation pathways. The formation of each fragment from the four molecules under study here will be discussed below.

3.1. Pyrimidine (C$_4$H$_4$N$_2$)

Pyrimidine, a C_{2v} symmetry group molecule, is isoelectronic with benzene. Indeed, calculations of various aromaticity indices show no substantial difference in aromaticity between these two species [37]. We first measured the photoionization mass spectrum of pyrimidine excited with 20 eV photons (Fig. 2). This spectrum is similar to that of the 70 eV electron impact mass spectrum [30] but shows evidence of less energy deposition since the $m/z = 51$ ion is absent and in the $m/z = 42–45$ range only the $m/z = 43$ ion appears in the 20 eV photon impact mass spectrum. The photoion yield curves were then investigated for each of the principal ion masses.

$m/z = 80$: We measured an adiabatic ionization energy of 9.21 ± 0.05 eV (Fig. 3, Table 1) for the parent ion. This is lower than the PIMS value (9.35 ± 0.05 eV) of Yencha and El-Sayed [38] and re-
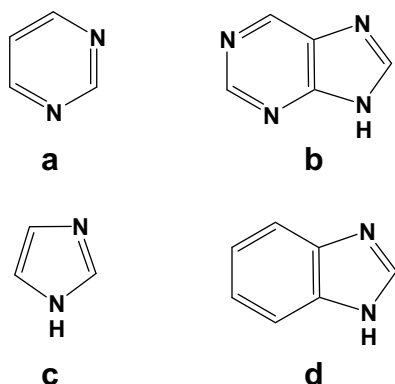

Fig. 1. Structures of nitrogen heterocycles investigated: (a) pyrimidine, (b) 9H-purine, (c) imidazole, (d) benzimidazole.
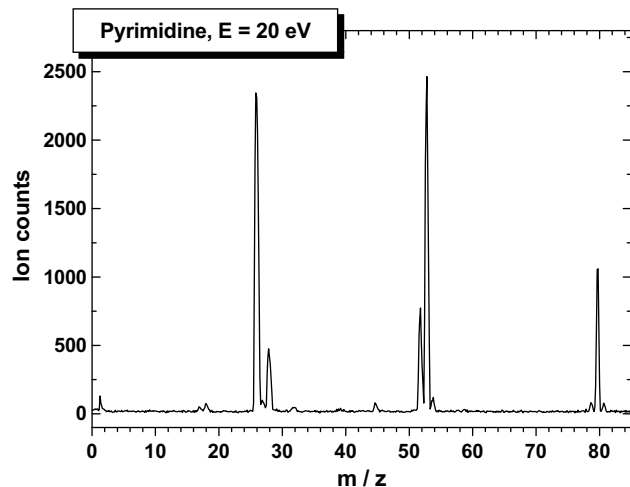
Fig. 2. 20 eV Photon impact mass spectrum of pyrimidine.

Fig. 3. Photoion yield curves of the pyrimidine parent cation and three of its fragment ions.

flects the higher detection sensitivity of our instrument. Photoelectron spectral values of the adiabatic IE listed in the NIST compilation [30] vary between 9.1 eV [39] and 9.42 eV [40], while the vertical ionization energies are of the order of 9.73 eV. An adiabatic value of 9.23 eV, close to our measured PIMS value of 9.21 ± 0.05 eV, and a vertical value of 9.73 eV, have been reported in the 21.21 eV photoelectron spectrum study of Gleiter et al. [41]. Asbrink et al. [42] have given 9.32 ± 0.01 eV as the adiabatic, and 9.7 eV as the vertical values, measured by 121.5 nm photoelectron spectroscopy, whereas IE(vert) = 9.8 eV is given in the recent PES study of Potts et al. [24]. Fig. 3 shows that 9.7 and 9.8 eV are far from the onset of the parent photoion yield curve.

The difference between adiabatic and vertical ionization energies is thus of the order of 500 ± 100 meV. In the nucleobases adenine, thymine and uracil, the corresponding energy differences are respectively 250 ± 30, 300 ± 100 and 440 ± 90 meV [5]. Differences between adiabatic and vertical energies correspond to nuclear reorganization energies and so reflect changes in the bond lengths and bond angles between the ground states of the neutral and the
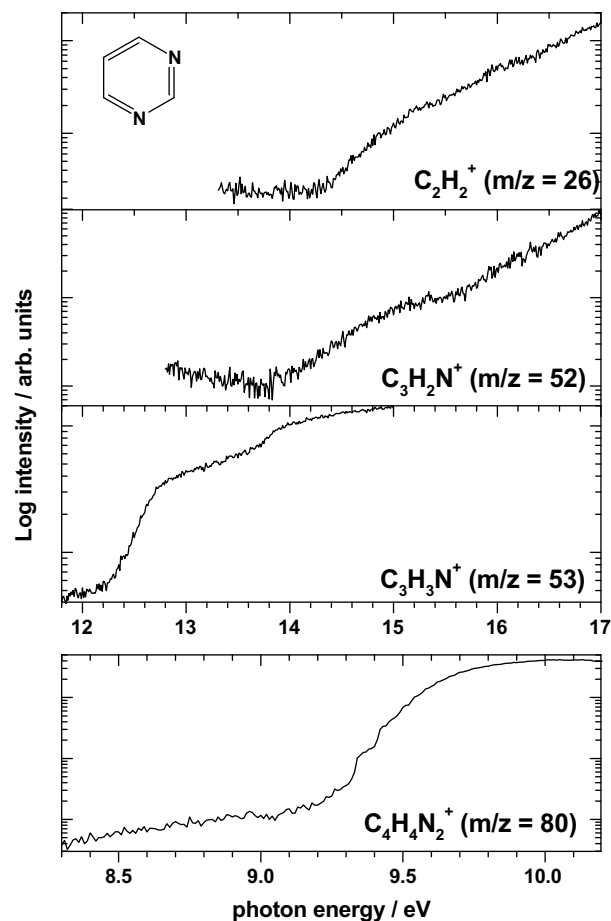
cation. These result in Franck–Condon transition shifts, as confirmed by theoretical calculations on the nucleobases, discussed elsewhere [5]. The vertical and adiabatic (0–0) ionization energies

Table 1
Pyrimidine ($C_4H_4N_2$) appearance energy measurements and possible fragmentation products

m/z	AE/eV	Possible fragment cation m_1^+	Neutral fragments process assignments in bold	Apparent $\Delta_f H_{gas}(m_1^+)$/eV	Literature value $\Delta_f H_{gas}(m_1^+)$/eV ion assignments in bold
80 (Parent ion)	9.21 ± 0.05 (IE)			11.24 ± 0.07	$C_4H_4N_2^+$: 11.36 ± 0.07
79	[a]	$C_4H_3N_2^+$	**H**	⩽12.78 ± 0.02	$C_4H_3N_2^+$:[b]
54	⩾11 eV[a]	$C_2H_2N_2^+$	**C_2H_2**	⩽10.68	$C_2H_2N_2^+$:[b]
		$C_3H_4N^+$	CN	⩽8.52	$C_3H_4N^+$: see text (CH_2CHCNH^+): 9.534
53	12.27 ± 0.05	$C_3H_3N^+$	**HCN**	12.90 ± 0.07	$C_3H_3N^+$:**12.77 ± 0.01**[c]
		$C_2HN_2^+$	C_2H_3	11.2 ± 0.12	$C_2HN_2^+$:[b]
52	13.75 ± 0.1	$C_3H_2N^+$	**HCN + H**	12.12 ± 0.1	$C_3H_2N^+$:[b]: ⩽12.14 see text
			H_2CN	13.4 ± 0.5	
		$C_4H_4^+$	N_2	15.78 ± 0.12	$C_4H_4^+$: 12.64 ± 0.02[d]
		$C_2N_2^+$	C_2H_4	15.24 ± 0.12	$C_2N_2^+$: 16.573 ± 0.01
			$C_2H_3 + H$	10.42 ± 0.17	
			$C_2H_2 + H_2$	13.43 ± 0.12	
28	13.52 ± 0.10	$HCNH^+$	C_3H_2N $HCN + C_2H$	9.20 ± 0.10	**$HCNH^+$: 9.813**
		$C_2H_4^+$	C_2N_2	12.35 ± 0.10	**$C_2H_4^+$: 11.059**
26	14.2 ± 0.2	$HCCH^+$	**2HCN**	13.43 ± 0.22	**$C_2H_2^+$: 13.75**
			$N_2 + C_2H_2$	13.87 ± 0.22	
		H_2CC^+	2HCN	13.43 ± 0.22	H_2CC^+: 15.81
		CN^+	$H + HCN + C_2H_2$	10.22 ± 0.22	CN^+: 18.14 ± 0.05
			$HCN + C_2H_3$	11.73 ± 0.27	

Apparent enthalpies of formation have been calculated using values listed in Table 5.
[a] Very weak ion, AE determination difficult or not possible. See text.
[b] Standard enthalpy of formation is not available in the gas phase from the NIST standard reference data base.
[c] 2-Propenenitrile cation.
[d] 1-Butene-3-yne cation.

of pyrimidine have been calculated using coupled cluster response theory and unrestricted DFT B3LYP/cc-pVDZ [43], giving a difference of 490 meV, in excellent agreement with our measurements. In pyrimidine, Potts et al. [24] agree with Gleiter et al. [41], as well as Asbrink et al. [42] and Piancastelli et al. [39], that ionization, which involves removal of an electron from the $7b_2$ molecular orbital, concerns a non-bonding $n\sigma$ orbital on nitrogen. In all the other compounds studied here, ionization results from loss of an electron from a π orbital.

Using our IE = 9.21 eV we calculate the value for the enthalpy of formation of the pyrimidine cation to be 11.24 ± 0.07 eV. The IE values recommended in the NIST table [30] lead to a slightly higher value, 11.36 ± 0.07 eV.

Gleiter et al. [41], have proposed the following adiabatic ionization energies of electrons in specific molecular orbitals: 9.23 eV, $b_2(\sigma, n_-)$; 10.41 eV, $b_1(\pi, S)$; 11.10 eV, $a_1(\sigma, n_+)$; 11.39 eV (vert), $b_2(\pi, A)$; 13.51 eV, $b_1(\pi)$, where the $b_1(\pi)$ is derived from the a_{2u} orbital in D_{6h} benzene, and S and A are respectively the two π levels in C_{2v} pyrimidine derived from the degenerate e_{1g} orbital in benzene. Yu et al. [44] assign a 13.9 eV PES band to an a_2 symmetry orbital, which differs from the M.O. assignment of Potts et al. [24] (see later).

There are steps in the initial part of the parent ion yield curve, at 9.34 and 9.42 eV (Fig. 3), which we consider to reflect vibrational excitations in the ion. Their energy intervals from the onset at 9.21 eV are 130 meV (1049 cm^{-1}) and 210 meV (1694 cm^{-1}); the difference between these two values is 80 meV = 645 cm^{-1}. In the absorption spectrum of pyrimidine [20] a Rydberg state converging to the ion ground state exhibits excitation of the stretching v_1 (118 meV [45]) and in-plane deformation v_{6a} (77 meV [45])

vibrations, which are mirrored in the PES first band where there are reported vibrational intervals of 81, 122 and 150 meV, assigned respectively to v_{6a}, v_1 and v_{9a} [42]. Our PIMS 130 meV first interval can be assigned to the totally symmetric v_1 vibration, and the second interval to $v_1 + v_{6a}$. There are also steps in the ion yield curve at about 10.4 and 11.2 eV. The 10.4 eV feature coincides with the reported PES band at 10.4 eV [39,42,51]. Asbrink et al. [42] consider that this PES band has nonbonding character, assigned $2b_1$, π, with vibrational structure. The 11.2 eV step corresponds to the origin band of a PES feature $1a_2$, π, at about 11.1 eV, also considered as somewhat nonbonding by Asbrink et al.

If there were no σ–π interaction, a 6π radical cation would be generated at 9.23 eV and a 5π radical cation at 10.41 eV. These radical cations have different heats of formation $\Delta H_f(6\pi) = 260$ kcal/mol (11.27 eV), $\Delta_f H(5\pi) = 287$ kcal/mol (12.45 eV). In the 6π system, the charge is localised on the nitrogen atoms, whereas in the 5π system the charge is distributed on the ring. However, the close proximity of these two electronic states favours their interaction so that the fragmentation of the ion at higher energies would not be from isolated states but from the ground state in obeyance to the quasi-equilibrium theory of mass spectra.

Calculations on the pyrimidine hydrogen-shift isomers [46] show that four ylide ions (distonic radical cations) having a single N–H bond lie at less than 380 meV above the pyrimidine ion. These are obviously 6π ions formed by ionization of a lone pair at nitrogen, and hydrogen transfer. Using their calculated relative energies [46], we determine that the heats of dissociation of the four ylide cations which have a single N–H bond are, respectively 12.62, 12.79, 12.84 and 12.97 eV. The heat of formation of neutral pyrimidine is 2.029 eV (Table 5), so that these ylide cations could be
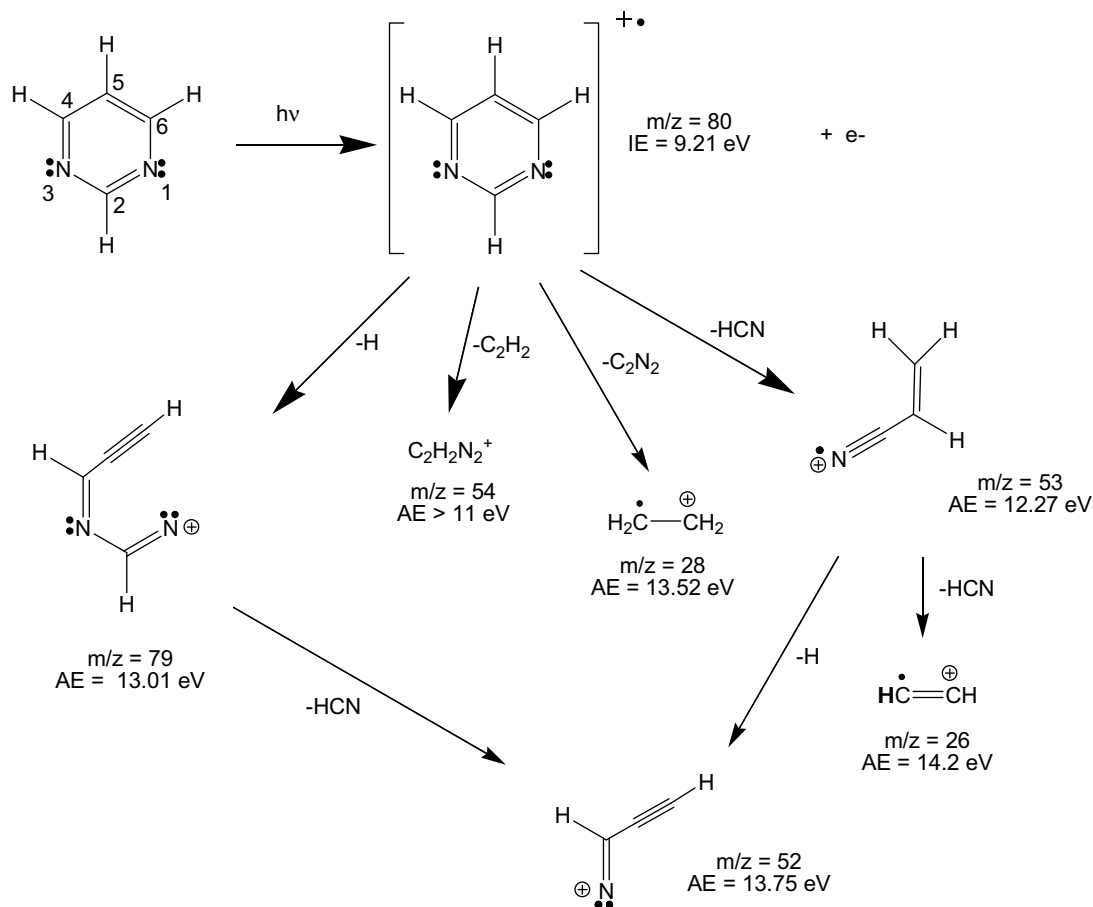

Fig. 4. Proposed principal fragmentation pathways in the VUV dissociative photoionization of pyrimidine.

accessible from the 6π radical cation above a photon excitation energy of 11 eV, i.e. in the range of the observed appearance energies of the fragment ions (see below and Table 1).

Major fragment ions are listed in Table 1 together with their apparent enthalpies of formation for various dissociation channels. Final ion assignments are in bold letters. Selected photoion yield curves from the pyrimidine measurements are shown in Fig. 3. Individual fragment ions are discussed below.

m/z = 79: The $m/z = 79$ fragment ion is formed by H-loss in the parent cation (Fig. 4). This dissociative photoionization channel is reported to be a very slow reaction, consistent with the fact that the $m/z = 79$ ion is very weak in electron impact (EI) mass spectra at various energies (16, 20, 70 eV) [27]. Milani-Nejad and Stidham [47], based on an EI mass spectrometry study of deuterated pyrimidines, and Asbrink et al. [42], both propose loss of H attached to C2. However, Rice et al. [27] proposed the loss of a hydrogen atom attached to C5, which would require rearrangement, therefore agreeing with a slow reaction.

Because of its weakness, the appearance energy of this ion fragment could not be measured in our PIMS investigation. An EI appearance energy measurement is reported to be 13.01 ± 0.1 eV [26]. This leads to an upper limit of 12.78 ± 0.02 eV for the heat of formation of the $C_4H_3N_2^+$ ion. A charge exchange mass spectrum of pyrimidine [42] provided an AE ≈ 13.6 eV for the $m/z = 79$ ion.

We note that not only is the yield of the H-loss ion low, but also there is virtually no ($m/z = 78$) ion corresponding to a molecular hydrogen (H_2) loss channel. These observations are in marked contrast to the fragmentation behaviour of the isoelectronic species benzene. The dominant channel leading to loss of an H-atom in the benzene cation corresponds to a dissociation energy of 3.88 eV [48]. In pyrimidine, the comparable dissociation energy has an upper limit of 3.8 eV, and is thus similar to that of benzene. It is probable that, in pyrimidine, the competitive HCN loss channel, producing the $m/z = 53$ ion (see later) is faster than that of the H-loss channel, thus leading to a low yield of the $m/z = 79$ ion. Concerning the H_2 loss channel, it is remarkable that this is also a negligible channel in pyridine, which is also isoelectronic with benzene. Ionization from a heteroatom in the azines thus leads to markedly different fragmentation processes as compared with ionization of a π electron in an all carbon system.

m/z = 54: This ion is also very weak and its appearance energy could not be measured. However, the ion signal was only observed above 11 eV. We assign this ion as $C_2H_2N_2^+$, with an apparent enthalpy of formation $\Delta_f H\,(C_2H_2N_2^+) \leqslant 10.68$ eV, formed by loss of acetylene ($m = 26$). Assuming cleavage of only two bonds, N3–C4 and N1–C6, the atom sequence should be N–CH–N–CH. The calculated lowest energy $C_2H_2N_2$ neutral is the van der Waals dimer HCN...HCN, while the lowest chemically bound (i.e. not H-bond complexed) $C_2H_2N_2$ neutral has the structure HNC(H)CN [49]. No literature value of the enthalpy of formation is available for $C_2H_2N_2^+$.

The alternative $m = 26$ loss species is the CN radical, giving rise to the $C_3H_4N^+$ ion, but this is less probable since it represents a pathway more endothermic by 2.16 eV (see Tables 1 and 5). Furthermore, the apparent heat of formation, $\Delta_f H\,(C_3H_4N^+) \leqslant 8.52$ eV, is less than the calculated values for a set of 23 different $C_3H_4N^+$ isomers, of which the six most stable have $\Delta_f H$s in the range 9.59–11.24 eV [50]. An experimental value $\Delta_f H(C_3H_4N^+) = 9.534$ eV is listed for the propenaldimine-1-yl cation (CH_2CHCNH^+) [29].

m/z = 53: This strong ion $C_3H_3N^+$ corresponds to the loss of HCN from the parent cation. The alternative possible loss of C_2H_3 as $m = 27$ would make $C_2N_2H^+$ as the $m/z = 53$ ion. This can be excluded from our measured AE = 12.27 ± 0.05 eV, giving $\Delta_f H(C_2N_2H^+) = 11.2$ eV, which is considerably lower than the literature value, 12.03 eV, for this ion [29]. The AE for the $m/z = 53$ ion

is in the Frank–Condon gap which exists in the photoelectron spectrum between 12.1 and 13.6 eV [42]. The corresponding dissociative photoionization process must therefore involve autoionization.

There are changes of slope in the $m/z = 53$ yield curve at 12.65 and 13.76 eV. The former is in the Franck–Condon gap, whereas 13.76 eV is close to the vertical energy of the ion state at 13.9 eV [24] and so may be at about the adiabatic energy for this state. It is also identical with the onset for $m/z = 52$ (13.75 ± 0.1 eV) (see below). The PES band at 13.9 eV is considered by Potts et al. [24] as corresponding to electron ejection from 2 (possibly 3) M.O.s, the innermost π orbital ($1b_1$) and two ordinary σ-type orbitals $6a_1$ (and $4b_2$) [24]. The corresponding three ion states would then be 2^2B_1, 2^2A_1, 2^2B_2.

We remark that our measured appearance energy of the $C_3H_3N^+$ ion is 0.5 eV lower than that previously reported by Momigny et al. [26], 12.87 ± 0.10 eV, in their EI study of pyrimidine. Buff and Dannacher [51] carried out a PEPICO study on pyrimidine that showed the critical energy for loss of HCN in the ion to be of the order of 2.73 eV. This would correspond to an AE($C_3H_3N^+$) ≈ 12 eV. Our AE = 12.27 ± 0.05 eV provides $\Delta_f H_{gas}^{\circ}\,(C_3H_3N^+) = 12.90 \pm 0.07$ eV. This coincides nicely with the tabulated enthalpy of formation of the acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$) cation, 12.82 ± 0.01 eV [29]. At first sight, this suggests that the $C_3H_3N^+$ formed by dissociative photoionization of pyrimidine is the acrylonitrile cation, as indicated in Fig. 4, with the difference of 80 ± 80 meV in the enthalpies of formation reflecting the existence of some thermal energy deposited in the fragment ion.

A similar suggestion that this is the acrylonitrile ion was made by Buff and Dannacher [51]. These authors considered two models for HCN loss: (i) Model A, a concerted reaction involving ring breaking and simultaneous ejection of HCN; (ii) Model B, a rate-determining isomerisation to a suitably linear $C_4H_2N_2^+$ isomer, followed by the rapid cleavage of a terminal HCN moiety. The derived 0 K AEs are 11.95 and 11.97 eV, respectively. Their calculated AE for the acrylonitrile ion is 12.108 eV, whereas we observed AE = 12.27 ± 0.05 eV for $m/z = 53$. One can envisage two cases of a two-step formation of $m/z = 53$. (a) (i) rupture of N1–C2, followed by (ii) C5–C6: this gives an isonitrile form; (b) (i) rupture of N1–C2, followed by (ii) C4–N3: this gives a nitrile form, i.e. acrylonitrile. Lavorato et al. [46] measured the CID mass spectrum of acrylonitrile and reported it to differ substantially from those on pyrimidine and its H-shift isomers, although these differences appear to be minor in the published spectra of their Fig. 2.

Other isomeric structures are conceivable for the $m/z = 53$ ion. An EI mass spectrometric study of pyrimidine and a set of deuterated pyrimidines suggests that the loss of HCN principally involves the C4 carbon atom rather than C2, which led Milani-Nejad and Stidham [47] to assign $m/z = 53$ as $HC^{\cdot}{=}CH{-}N^{\cdot+}{=}C^{\cdot}H \leftrightarrow HC^{\cdot+}{=}CH{-}N{=}C^{\cdot}H$ [47]. More conventional conceptions would give $HC^{\cdot}{=}CH{-}N{=}C^+H \leftrightarrow HC^+{=}CH{-}N{=}C^{\cdot}H$. We note also the results of Lavorato et al. [46], who calculated that $H_2C{=}C{=}C{=}NH^{\cdot+}$ is 0.564 eV more stable than $CH_2{=}CH{-}C{\equiv}N^{\cdot+}$ (acrylonitrile). They also report that calculated isomers $H{-}C{\equiv}C{-}CH{=}N{-}H^{\cdot+}$ and $H{-}C{=}CH{-}C{=}N{-}H^{\cdot+}$ are higher in energy by 0.737 and 0.260 eV respectively. In our opinion the assignment of $m/z = 53$ remains an open question. Quantum chemical calculations on the structure and stability of the $C_3H_3N^+$ ion could be useful to further elucidate this question. Suitable H-shift possibilities in the proposed $m/z = 53$ structures should also be considered.

We remark that in isoelectronic benzene, the most important dissociation channel analogous to that of HCN loss in pyrimidine is to $C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2$ [52] (see later).

m/z = 52: This strong ion is assigned as $C_3H_2N^+$. Its appearance energy, 13.75 ± 0.1 eV, is 1.25 eV lower than that reported by Momigny et al. [26] in their EI MS study. On the basis of our AE

value, we calculate the enthalpy of formation $\Delta_f H^\circ_{gas}$ $(C_3H_2N^+) =$ 12.12 ± 0.1 eV, assuming loss of HCN and H. The two channels, initial loss of HCN then of H, and initial loss of H followed by HCN, are both active, as evidenced by the appropriate metastable ions in EI impact mass spectrometry [27]. Loss of H_2CN or its isomer HCNH from the parent cation is less probable since these are more endothermic radicals and, moreover, their formation would require rearrangement of at least one H atom. In the case of direct H_2CN loss from the parent cation, our AE would lead to $\Delta_f H^\circ_{gas}$ $(C_3H_2N^+) = 13.4 \pm 0.5$ eV. Our value $\Delta_f H^\circ_{gas}$ $(C_3H_2N^+) = 12.12 \pm$ 0.1 eV is in good agreement with the upper limit value determined by Willett and Baer [53], $\Delta_f H^\circ_{gas}$ $(C_3H_2N^+) \leqslant 12.14$ eV. The Lias et al. compilation [29] gives $\Delta_f H^\circ_{gas}$ $(C_3H_2N^+) = 11.684$ eV from proton affinity data.

Loss of H from $m/z = 53$ is the most probable $m/z = 52$ forming reaction between 13.75 and 14.2 eV, the latter energy being the appearance onset for $m/z = 26$, corresponding to the loss of a second HCN molecule (see later). The decay of the $m/z = 53$ ion and the simultaneous quasi-parallel rise of $m/z = 26$ and $m/z = 52$ is confirmed by the charge exchange mass spectra of pyrimidine measured by Asbrink et al. [42].

Milani-Nejad and Stidham [47] suggest for the two two-step channels in the formation of the $m/z = 52$ cation, (i) first loss of C4 in a HCN loss channel followed by loss of H attached to C2. (ii) First loss of H attached to C2 followed by loss C4 in HCN loss. They propose $m/z = 52$ as $HC\dot{=}CH-N\dot{=}C^+ \leftrightarrow HC^+=CH-N\equiv C\ddot{\,}$.

One alternative assignment for $m/z = 52$ is $C_2N_2^+$ (Table 1). Our AE for $m/z = 52$ is not compatible with this assignment since it leads to apparent heats of formation much smaller than that known for $C_2N_2^+$ (Table 1). Another possibility is loss of N_2 to give the $m/z = 52$ ion $C_4H_4^+$. This channel, which would be the exact equivalent of the important $C_4H_4^+ + C_2H_2$ dissociation in the benzene cation [52] has been considered by Buff and Dannacher [51]. The expected appearance energy in pyrimidine for the $m/z = 52$ $C_4H_4^+$ ion lies between 10.35 and 10.77 eV, according to the particular $C_4H_4^+$ structure. This is very much lower than our observed AE for the $m/z = 52$ ion and so excludes this assignment.

$m/z = 28$: The appearance energy of this strong fragment ion is 13.52 ± 0.10 eV. We first consider that it is $HNCH^+$, which is more stable than its non-linear isomers CNH_2^+ and NCH_2^+ by about 1.94 eV and 3.12 eV, respectively according to calculations of Conrad and Schaefer III [54]. The concomitant neutral loss of C_3H_2N would make this the charge switch reaction with respect to the direct loss channel forming $m/z = 52$. This reaction giving $m/z = 28$ would require a H-shift, whereas the ionic ylides could dissociate to the $HNCH^+$ ion by a direct bond cleavage reaction.

In the Rice et al. EI study at 16, 20 and 70 eV, the ions $m/z = 28$ and 52 have approximately the same intensity ratio [27]. We note that they have similar AEs in our PIMS study. If the neutral products are HCN and C_2H, the derived apparent heat of formation of $HNCH^+$ becomes 9.20 ± 0.15 eV, which is less than the literature value 9.813 eV [29]. Thus a single neutral product appears probable, namely C_3H_2N. Its formation would require H atom migration to a nitrogen atom, forming an ylide cation and rupture either of a carbon–carbon and a carbon–nitrogen bond or of two carbon-nitrogen bonds, according to the particular ylide structure. From the calculated energies of the transition states leading to the two most probable ylides [46], their formation could occur at 11.93 eV and 12.14 eV respectively, i.e. 1.59 eV and 1.38 eV below the appearance energy of $m/z = 28$.

In Fig. 4 we give another possible assignment of the $m/z = 28$ ion. This is the ethylene cation $C_2H_4^+$, with concomitant loss of cyanogen C_2N_2. From our AE value this pathway leads to $\Delta_f H(C_2H_4^+) = 12.35 \pm 0.01$ eV, higher than the literature value $\Delta_f H(C_2H_4^+) = 11.059$ eV (Table 5). The formation of $C_2H_4^+$ from $m/z = 53$ by loss of C_2H is improbable.

$m/z = 26$: The yield curve of this ion has slight inflexions at 14.57, 14.83, 15.19 and 15.86 eV. We note that there are PES peaks at 14.4, 15.8 eV corresponding to σ states according to Potts et al. [24]. These would be the 2^2B_2 and 3^2A_1 ion states of the pyrimidine cation.

The strong $m/z = 26$ fragment ion (AE = 14.2 ± 0.2 eV) is assigned to $C_2H_2^+$, presumably formed by successive loss of two HCN molecules. Multiple HCN loss also occurs as important processes in adenine [5]. From our AE = 14.2 ± 0.2 eV we calculate $\Delta_f H(C_2H_2^+) = 13.427 \pm 0.2$ eV. The literature value is 13.749 eV. In searching to understand the difference between these values we considered whether the $C_2H_2^+$ species was the vinylidene cation, H_2CC^+, rather than the acetylene ion $HCCH^+$. For neutral vinylidene, $\Delta_f H(H_2CC) = 4.384 \pm 0.24$ eV [55], so that our $\Delta_f H(C_2H_2^+) =$ 13.427 ± 0.2 eV. This implies I.E.$(H_2CC) = 9.043 \pm 0.44$ eV. The latter is much smaller than a recent calculated value I.E.$(H_2CC) =$ 11.26 eV [56]. Furthermore, Hayakawa et al. [57] derive $\Delta_f H(H_2CC^+) = 15.81$ eV. This high $\Delta_f H$ for the vinylidene cation also excludes this species as an assignment for the $m/z = 26$ ion.

We also considered a process where the acetylene cation is formed by loss of N_2 and C_2H_2 from the parent cation. This is thermodynamically allowed, giving rise to a very reasonable value of $\Delta_f H(C_2H_2^+) = 13.866$ eV from the $m/z = 26$ appearance energy but it is kinetically less probable since rearrangement is required to form N_2. Finally we consider that $H_2C_2N_2$ could be lost as a single product from the parent ion. However, in order to evaluate this, we require a knowledge of the $\Delta_f H$ of the HCN dimer, but this is not available.
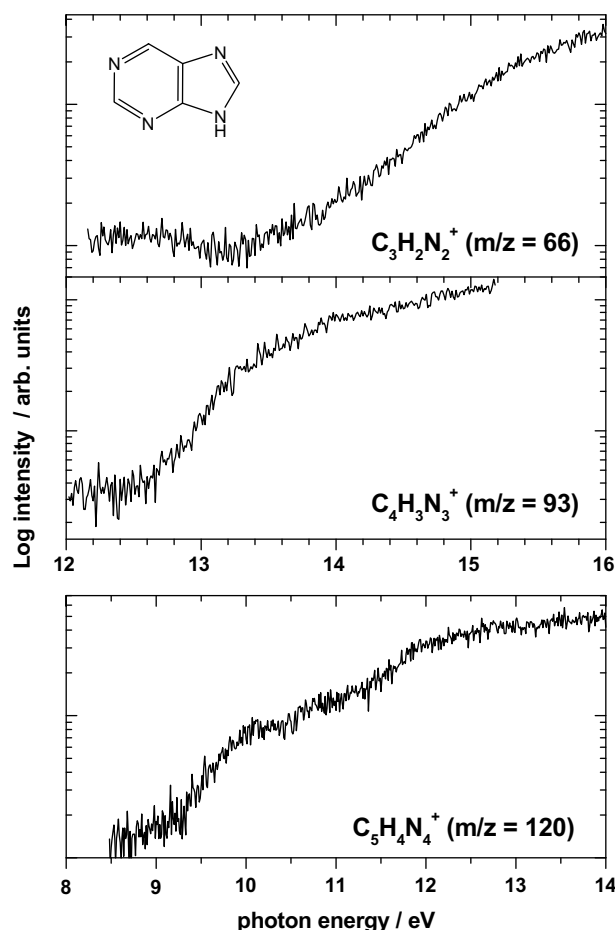

Fig. 5. Photoion yield curves of the purine parent cation and two of its fragment ions.

An alternative assignment of $m/z = 26$ to CN^+ is dismissed by the much too low apparent heat of formation as compared with the known $\Delta_f H(CN^+) = 18.14 \pm 0.05$ eV (Table 5).

The VUV induced fragmentation behaviour of pyrimidine is summarized in Fig. 4.

3.2. Purine ($C_5H_4N_4$)

Purine is indeed adenine without the NH_2 group. It has many tautomers but Lin et al. [58] have shown that the N(9)H tautomer is the most stable in gas phase (as it is in the case of adenine) and so is to be expected as the major tautomer in our study. The principal masses, relative abundances greater than 10%, in our 21 eV mass spectrum (not shown) are at $m/z = 120, 93, 66$. This is similar to the 70 eV EI-MS [30].

$m/z = 120$: This is the parent ion, whose IE = 9.35 ± 0.05 eV (Fig. 5). The estimated $\Delta_f H$(neutral $C_5H_4N_4$) = 2.383 eV [29]. From our AE we thus obtain $\Delta_f H(C_5H_4N_4^+) = 11.733 \pm 0.05$ eV. An estimated limiting value given by Lias et al. [29] is $\Delta_f H (C_5H_4N_4^+) \leqslant 11.91$ eV.

Literature values of the IE of purine are all for vertical ionization, and are derived from electron impact [25], photoelectron spectroscopy [21,24,58] and photoionization [25] studies. Values are in the range 9.52–9.7 eV. We consider our IE = 9.35 ± 0.05 eV as being the adiabatic, or close to the adiabatic, value. The difference between adiabatic and vertical IE values is thus in the range 170–350 meV. This is of the same order of magnitude as the corresponding difference, 250 ± 30 meV, in adenine, indicating

that in purine, too, there are neutral to ion structural changes leading to the Franck–Condon shift. We remark that the initial ionization region of purine has a more complicated molecular orbital parentage than does pyrimidine, which has clearly a well separated π^{-1} level, whereas there are close-lying π and $n\sigma$ orbital ionizations in the case of purine [24].

The fragmentation of the purine cation is mainly due to HCN and 2HCN loss processes. Fragments corresponding to the H, C_2H_2, HCN + H, and C_3H_2N loss processes observed in pyrimidine, do not occur in purine. In particular we note that, from an examination of the relevant structures, the absence of a H-loss process in purine cation fragmentation points to the loss of H in pyrimidine from positions 5 or 6, and in imidazole (see later) from positions 4 or 5. In purine these are the positions where both systems (imidazole and pyrimidine) are connected.

$m/z = 93$: This ion has an AE = 12.6 ± 0.05 eV. We assign it to $C_4H_3N_3^+$, with concomitant loss of HCN. The apparent heat of formation of $C_4H_3N_3^+$ is 13.58 ± 0.08 eV. There are no reported values of this quantity. A possible reaction pathway is by rupture of the two carbon-nitrogen bonds in the pentagon (C5–N7 and C8–N9). Another possibility is the rupture of two carbon-nitrogen bonds in the hexagon, as occurs in adenine [5]. This process has been proposed as the principal pathway in purine by Tatematsu et al. [59] on the basis of deuterium isotope electron impact mass spectral studies. The channel involving rupture of N1–C2 and C4–N3 (42%) and that involving C5–C6 and N1–C2 (34%) are competitive in the EI study. This leads to a substituted imidazole cation (Fig. 6), in contrast to the case of pyrimidine where loss of HCN
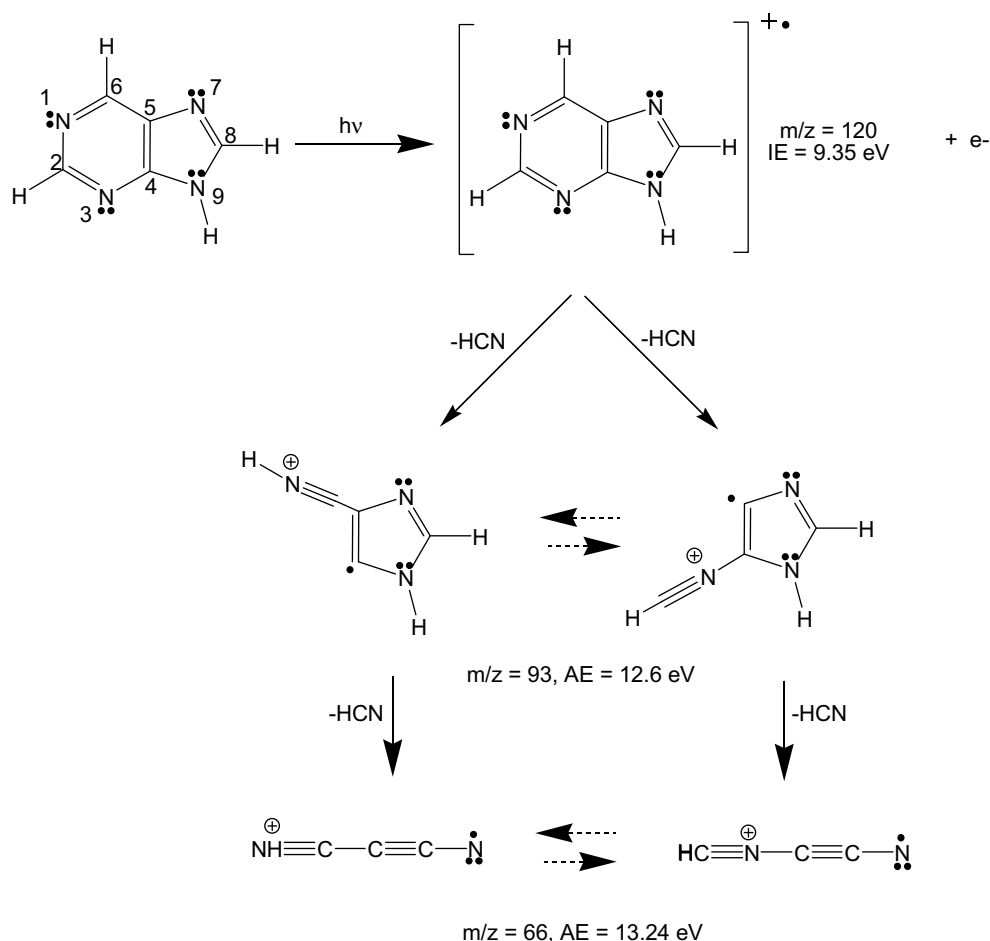

Fig. 6. Proposed principal fragmentation pathways in the VUV dissociative photoionization of purine.

produces a linear cation (Fig. 4). This substituted imidazole has a rather stable ring. At higher energies it loses a second HCN (see below), which is stable within the energy range of our measurements.

The alternative assignment of $C_3HN_4^+$ for $m/z = 93$, with C_2H_3 as neutral loss product, is inconsistent with the deuterium isotopic study of Tatematsu et al. [59].

$m/z = 66$: This fragment ion has an AE = 13.24 ± 0.1 eV and we assign it to $C_3H_2N_2^+$, formed by loss of 2HCN. This AE is only 640 meV above that for loss of a single HCN, whereas in pyrimidine the corresponding energy difference for loss of two, with respect to a single, HCN species is 1930 meV (Table 1). The apparent heat of formation of $C_3H_2N_2^+$ is 12.82 ± 0.13 eV. The malononitrile cation's heat of formation 15.56 ± 0.1 eV, so this ion can be excluded as $m/z = 66$. Three other structures can be conceived for $C_3H_2N_2^+$, (i) $HN^+{\equiv}C{-}C{\equiv}N{\cdot}{-}H$, (ii) $HC{\equiv}N^+{-}C{\equiv}C{-}N{\cdot}H$, (iii) $HN{\cdot}{-}C{\equiv}C{-}N^+{\equiv}CH$, the latter being formed via a cyclic structured $C_3H_2N_2^+$ issuing (directly) from the parent ion by rupture of the two bonds C5–C6 and C4–N3 and thus implying a neutral loss of $C_2H_2N_2$. Our study on the dissociative ionization of adenine [5], in which a fragment ion $m/z = 66$ is observed, provided three possible values for the heat of formation of a $C_3H_2N_2^+$ ion, 12.56, 11.56 and 11.20 eV, according to the respective heats of formation of the three isomeric NH_2CN species (cyanamide, diazomethane, 3-H-diazirine) that could be formed in the process creating $C_3H_2N_2^+$. Tatematsu et al. [59] propose (i) and (ii) as the $C_3H_2N_2^+$ fragment ion products but also consider that their deuterium isotopic study does not exclude participation of the third possibility, i.e. rupture of the C5–C6 and C4–N3 bonds in the parent ion, to form the $m/z = 66$ dehydroimidazole radical ion which rearranges to the final product ion.

We remark that an alternative assignment of $m/z = 66$ is to $C_2N_3^+$, with loss of $HCN + C_2H_3$. This assignment is inconsistent with the results of the EI-MS deuterium isotope substitution study of Tatamatsu et al. [59].

A schema of fragmentation processes in the dissociative photoionization of purine is shown in Fig. 6.

3.3. Imidazole $C_3H_4N_2$

Imidazole (C_s molecule) is related to both purine and adenine, being their pentagon part. Its dissociative ionization properties are thus interesting to compare with these two species. In imidazole, which is a five-membered ring with 6π electrons, the HOMO is a π molecular orbital; the ring is not completely planar because N1 is sp^2, whereas N3 is sp^3. The N–H bond is polar and less stable than the C–H bonds.

The imidazole ion states and their vertical energies (eV), as determined by photoelectron spectroscopy [60] are as follows: 8.78 ($1^2A''$, π), 10.3 ($2^2A''$, π; $1^2A'$, σ), 13.7 ($2^2A'$, σ), 14.0 ($3^2A'$, σ), 14.7 ($3^2A''$, π), 15.3 ($4^2A'$, σ), 17.9 ($5^2A'$, σ) eV.

Our mass spectrum at 21 eV is given in Fig. 7. The weakness of the parent ion at $m/z = 68$ is due to the mass discrimination properties of our quadrupole mass analyzer. Lowering the mass resolution gives a marked increase in the relative intensities of the peaks at $m/z = 67$ and 68 (see Section 2). The relative intensities of the principal ion peaks at $m/z = 41$, 40 and 28 are very similar in our 21 eV photon and the 70 eV electron impact [30] mass spectra.

$m/z = 68$: The parent ion has an IE = 8.66 ± 0.03 eV (Fig. 8). Reported vertical ionization energy values are: PI IE(vert) = 8.81 ± 0.01 eV [28]; EI IE(vert) = 9.12 eV [61]; PES IE(vert) = 8.96 eV [22], 8.78 eV [60]. In the PIMS study by Main-Bobo et al. [28], who used a many-line hydrogen lamp as photon source, the photon wavelength resolution was 17 meV at 120 nm (10.33 eV). These authors argue that their observed 8.81 eV step in the parent ion yield curve correlates with the 8.78 eV photoelectron spectral peak observed by Cradock et al. in a PES study [60]. However, Cradock
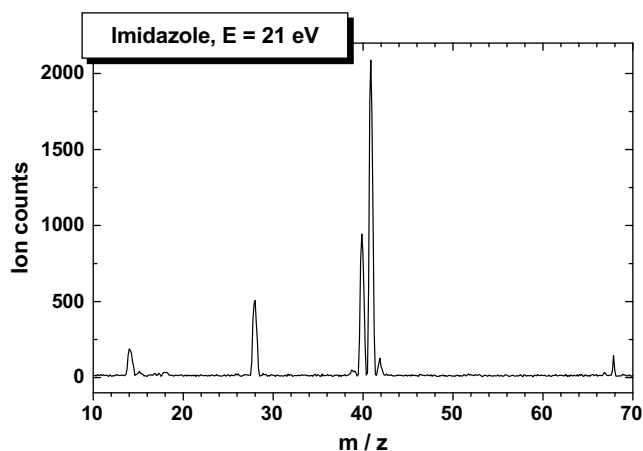

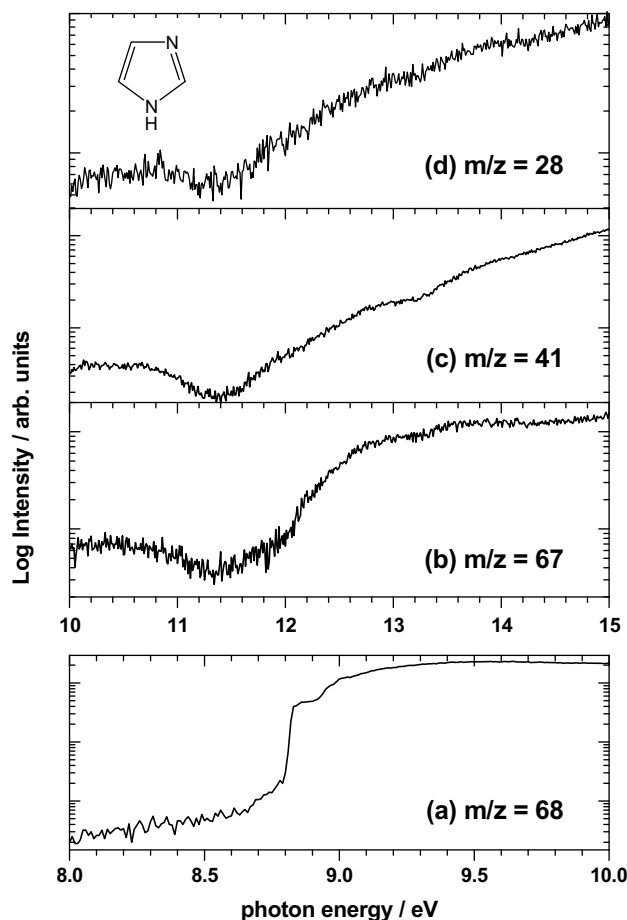**Fig. 7.** 21 eV Photon impact mass spectrum of imidazole.

Fig. 8. Photoion yield curves of the imidazole parent cation and three of its fragment ions.

et al. report this spectral peak as the vertical ionization value. Examination of published photoelectron spectra of imidazole [60] shows that the first ionization band has an extensive low-energy tail in the 8–8.7 eV region. We note that 8.81–8.66 = 0.15 eV = 1210 cm^{-1}, which is of the order of magnitude of several of the calculated molecular ion frequencies of $C_3H_4N_2^+$ [28]. We consider that we measure the adiabatic IE and that the Main-Bobo et al. value [28] is to be assimilated to vertical ionization values. The difference between the vertical and adiabatic IEs is therefore of

the order of 150 meV. This is a little smaller than the corresponding values in purine and adenine. Our I.E. value leads to determine the enthalpy of formation of the ion $\Delta_f H(C_3H_4N_2^+) = 10.04 \pm 0.03$ eV. The literature value, 10.31 eV [29], is based on I.E. = 8.81 eV.

Main-Bobo et al. [28] have shown that imidazole and pyrazole, which are isomers, do not have a common ion structure prior to dissociation. For imidazole, at the lowest IE = 8.66 eV, a 5π radical cation **2** (Fig. 9) is generated. At higher energies, hydrogen migration is possible, e.g. from N3 to C2 which leads to a radical cation
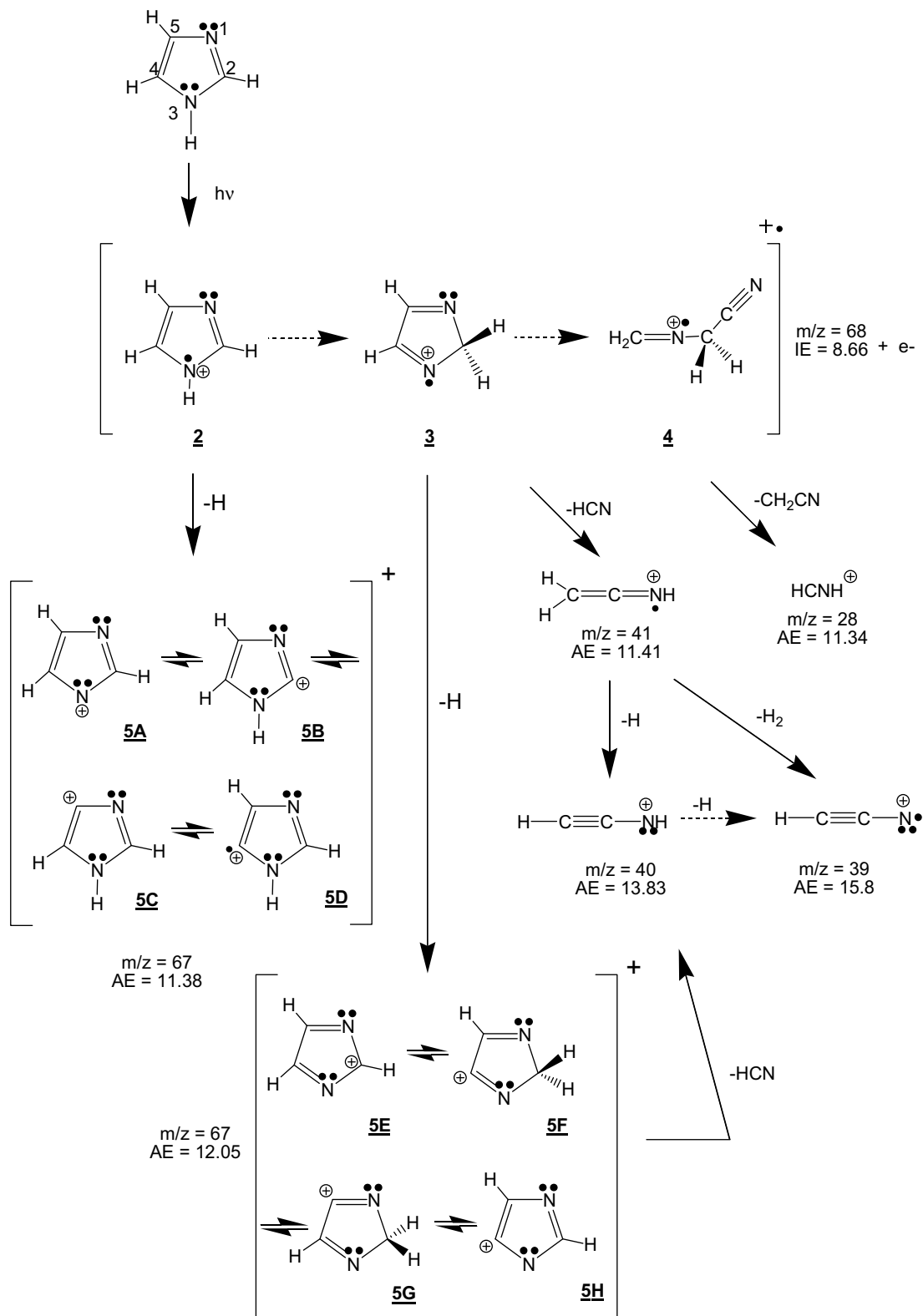

Fig. 9. Proposed principal fragmentation pathways in the VUV dissociative photoionization of imidazole.

with a 4π electron system and an unpaired σ electron. This is the diaza-cyclopentadienylium cation **3**. From this structure, ring-breaking can eventually lead to formation of the methyleneamino-acetonitrile radical cation **4** (Fig. 9) among other possible structures, and which might play a role in the fragmentation processes of imidazole.

Other H-shift processes are also possible. The imidazol-2-ylidene ylide of the imidazole cation, formed by 1,2-H shift, has been studied experimentally by [62], and both experimentally and computationally by McGibbon et al. [63], who also investigated the imidazol-4-ylidene cation. The calculated energy barriers between the imidazole cation and these two ylide ions are, respectively, 2.892 and 2.428 eV. If they play a role in our observed fragmentation processes their formation could be at 11.55 eV and 11.09 eV, respectively.

$m/z = 67$: We have assigned this fragment ion as $C_3H_3N_2^+$, formed by H-loss from the parent ion. The ion yield curve exhibits a weak signal whose onset is at 11.38 eV and a stronger signal beginning at 12.05 eV (Fig. 8, Table 3). These energies are both in a Franck–Condon gap region (11.3–13.1 eV) of the photoelectron spectrum of imidazole [60], so that excitation to autoionizing neutral states of imidazole must be involved. We considered whether the existence of two onsets for this reaction is related to H-loss from different positions. According to the deuterium isotopic EI MS study of Klebe et al. [61], there is a high degree of specificity for the loss of H from the 4(5) position. In their ion source, the loss of H appears to proceed much faster than hydrogen scrambling. It is possible that our first onset reflects H-loss from the 4(5) position and the second onset corresponds to a situation when H atom scrambling (perhaps leading to one of the structures, such as the ylides discussed above), becomes more efficient due to extra internal energy in the ion, even if it does not attain complete scrambling. Note that according to Klebe et al. [61] there is a disinclination of loss of H at the 2-position. C–H bond fission is much less prevalent when there are two adjacent N atoms to the C–H group, whereas positions 4 and 5 have only one N atom adjacent. (We note that in purine, the C–H group on the pentagon, which participates in the HCN loss process, has two adjacent N atoms).

The two AEs lead to two different apparent heats of formation, perhaps corresponding to the formation of two different isomers of $C_3H_3N_2^+$. Loss of a H atom in the 5π radical cation $C_3H_4N_2^+$ gives a system with one unpaired π electron and one unpaired σ electron which may be stabilized to a 6π cation, whose different possible structures, A–D, correspond to different positions of charge and H atoms (structures 5A–5D, Fig. 9). The different structures of $C_3H_3N_2^+$ generated after H-loss should have nearly the same energy. We recall, also, that the two N atoms differ in electron hybridization.

A second class of $C_3H_3N_2^+$ ions (structures E–H) can be generated from the 4π cation (Fig. 9). The antiaromatic cations E–H are higher in energy than A–D. Linear $C_3H_3N_2^+$ ions could also be formed if ring opening of $C_3H_4N_2^+$ occurs. We suggest that the two apparent AEs for the H-loss reaction, at 11.38 and 12.05 eV respectively, correspond respectively to A–D and E–H structures. The ions resulting from H-loss in $C_3H_4N_2^+$ are more stable than those produced by H-loss in the pyrimidine cation. This may be due to H-loss and HCN loss being parallel reactions in imidazole (see below), whereas in pyrimidine they are sequential loss reactions, with the second being faster than the first.

From our AE = 11.38 ± 0.05 eV we obtain an apparent $\Delta_f H = 10.56 \pm 0.06$ eV, while for AE = 12.05 ± 0.03 eV, the apparent $\Delta_f H = 11.17 \pm 0.04$ eV. Lias et al. [29] list 10.99 eV for the heat of formation of $C_3H_3N_2^+$ (NCCH$_2$CNH$^+$), from a proton affinity measurement. We note that for the $[M-H]^+$ ion, NIST [30] reports AE = 12.8 eV from the EI study of Klebe et al. [61]. However, their

IE = 9.12 eV for the parent molecule is 560 meV above our IE(ad), so that their AE for $(M-H)^+$ is also probably too high. We remark that Main-Bobo et al. did not measure the AE of the $[M-H]^+$ ion but they observed a bimodal KERD and a large kinetic energy release for this H-loss channel and they discuss metastable ion peaks for H-atom loss [28]. Main-Bobo et al. give KER T(1/2) = 250 meV, so that from our AE value, the $\Delta_f H(C_3H_3N_2^+)$ could be 10.56–0.25 = 10.31 eV. This is lower than the value 10.99 eV given by Lias et al. [29] for the heat of formation of $C_3H_3N_2^+$ (NCCH$_2$CNH$^+$) from a proton affinity measurement.

Main-Bobo et al. remark that in the electron impact mass spectrum of imidazole the yield of the $[M-H]^+$ ion is higher than in their PIMS study. They suggest that this is possibly due to autoionization via neutral triplet states which are formed by electron excitation but not by photon impact.

We note that there is a rising inflexion in the $m/z = 67$ yield curve at about 13.3 eV, close to the sharp increase in the PES signal at 13.2 eV, which is at the end of the Franck–Condon gap [60].

$m/z = 41$: This strong fragment ion is assigned to $C_2H_3N^+$ and is formed in a HCN loss channel. That the neutral product is HCN and not HNC has been shown by Main-Bobo et al. [28]. They also give structural and energy arguments in favour of $m/z = 41$ being CH_2CNH^+ rather than CH_3CN^+ or CH_3NC^+. Collision induced decomposition (CID) of the isomers imidazole and pyrazole demonstrated that it is the same $m/z = 41$ ion formed in both cases, yet no isomeric interconversion has occurred. Since pyrazole has two adjacent N atoms, formation of CH_2NCH^+ would require considerable atomic rearrangements, not supported by dissociation rate data; they therefore conclude that $m/z = 41$ ion is CH_2CNH^+ [28].

The reaction $C_3H_4N_{2+} \rightarrow C_2H_3N^+ (CH_2CNH^+)$ $(m/z = 41) + HCN$ involves a single 1,2 H-atom shift. Breaking of two of the C–N bonds leads to formation of HCN. This involves two parallel channels which should have two different transition state energies in their C–N bond breaking steps, since the bond energies differ: (i) rupture of N1–C5, H-shift from C4 to C5, rupture of C2–C3, losing HCN containing C2; (ii) rupture of N3–C2, H-shift C4–C5, rupture of C5–N1, losing HCN containing C2. Main-Bobo et al. observed that the $m/z = 41$ ion was formed with considerable KE release [28], involving large and small energy release components. They showed that $m/z = 41$ is a single daughter ion that is indeed produced via two transition states. On the basis of EI mass spectral studies of imidazole deuterated to various degrees and atomic positions, Klebe et al. [61] state that primarily positions 3 and/or 2 are involved in the elimination of HCN, possibly preferentially from position 2, which is that suggested by Main-Bobo et al. [28].

We remark that in uracil, following Rice et al. [27], we assigned the $m/z = 41$ ion as $HC=CHNH^+$ which is formed by a pathway appropriate to this nucleobase. Bowie et al. [64] have proposed that $m/z = 41$ is a cyclic ion, the 1*H*-azirine radical cation. In their EI-MS study, van Thuijl et al. [65] suggested that the $m/z = 41$ ion formed from imidazole is a mixture of open chain radical cations, of the $HC=CHNH^+$ type, probably interconvertible via the 1*H*-azirine radical cation. We suggest that at onset the $C_2H_3N^+$ ion has the structure $CH_2-C^+=NH$ (since $CH=N-CH_2^+$ can be eliminated, see below) remarking that at higher energies the structure of the molecular radical cation $C_3H_4N_2^+$ may have changed and that products with another structure might appear. Simultaneous ring opening in the cyclic educt ion cannot be excluded, in which case triplet as well as singlet $C_2H_2N^+$ can be formed, so that the triplet state should also be taken into account.

The measured appearance energy of the $m/z = 41$ fragment ion is AE = 11.41 ± 0.05 eV (Fig. 8). A PIMS value of 11.48 ± 0.02 eV was reported by Main-Bobo et al. [28]. These values are much lower than the 13.2 eV reported in the EI study of Klebe et al. [61].

From the photoelectron spectrum [60] we can deduce that this fragment ion is formed in a Franck–Condon gap region, thus essentially by photon excitation to autoionizing neutral electronic states of imidazole.

Our measurements give the apparent $\Delta_f H(C_2H_3N^+) = 11.39 \pm 0.06$ eV. The KER reported by Main-Bobo is T(1/2) = 55 meV [28], so that the apparent $\Delta_f H$ could be 11.39–0.055 eV = 11.33 eV. The isomeric $C_2H_3N^+$ ions acetonitrile and methylisocyanide have $\Delta_f H$ values that are respectively 12.97 eV and 12.9 eV [30], so that $m/z = 41$ ion cannot be either of these two species, thus giving additional confirmation that it is CH_2CNH^+. The experimental $\Delta_f H$ of $CH_2CNH^+ = 10.41 \pm 0.04$ eV [53], while $\Delta_f H(CH_2NCH^+) = 10.83$ eV according to the ab initio calculations reported by Main-Bobo et al.. Two other $C_2H_3N^+$ ions also have calculated $\Delta_f H$ values of the order of 13 eV, and so are also excluded. We consider our AE and derived $\Delta_f H$ values to be consistent with the $\Delta_f H(CH_2CNH^+) = 10.41$ eV of Willett and Baer [53].

We also considered CHN_2^+ as an assignment for $m/z = 41$, formed by loss of C_2H_3 from the parent ion (Table 3) but this is incompatible with the results of the deuteration study of Klebe et al. [61].

We note that in the $m/z = 41$ yield curve there are "steps" at 13.24 eV, which is where the Franck–Condon gap ceases, so that this is the beginning of a region where direct ionization can occur. It is also possible that this step is associated with the formation of the acetonitrile ion CH_3CN^+, whose calculated AE is 12.99 eV.

$m/z = 40$: The assignment of this ion is to $C_2H_2N^+$. The neutral products are HCN + H or H_2CN. The yield curve onset is smooth and the AE = 13.83 ± 0.05 eV. There is no previous report of this AE.

There are three conceivable processes for formation of this ion. (1) loss of H_2CN from the parent ion; (2) H-loss from CH_2CNH^+ ($m/z = 41$); (3) loss of HCN from $m/z = 67$ [M−H]+. Using the value $\Delta_f H(H_2CN) = 2.3859 \pm 0.43$ eV, which results from our analysis of the experimental and theoretical data concerning this entity discussed by Nesbitt et al. [66], we evaluate $\Delta_f H(C_2H_2N^+) = 12.82 \pm 0.43$ eV for the first process (loss of H_2CN). The energy difference between the AE's of $m/z = 40$ and 41 is 2.41 eV. This is a reasonable value for a H-loss process (second process, H-loss from $m/z = 41$). The energy difference between the AE's of $m/z = 40$ and 67 is 2.45 eV (third process, HCN loss from $m/z = 67$). Since the precursor ions $m/z = 67$ and 41 have very similar AEs, the two channels to form these ions are competitive. This is consistent with the observation that the ratio of the m/z (67/41) ion intensities is constant over the considerable electron energy range 12–70 eV in EI mass spectra [61].

Our apparent $\Delta_f H(C_2H_2N^+) = 11.55 \pm 0.06$ eV is smaller than the value 12.82 ± 0.43 eV given above (loss of H_2CN channel) and the 12.58 eV value listed in Lias et al. [29] for the CH_2CN^+ ion. Harland and McIntosh [67] report $\Delta_f H = 12.497 \pm 0.052$ eV for H_2CNC^+ and 13.026 ± 0.052 eV for H_2CCN^+, while Anich et al. [68] give $\Delta_f H = 12.49$ eV for H_2CNC^+ and 13.01 eV for H_2CCN^+. Other structures can also be proposed for $C_2H_2N^+$ [5]: (i) a quasi-linear $HN=C=C^+H$ or $H-C=CN^{+\cdot}H$ (as in our Fig. 9) and (ii) a cyclic structure in which a N atom is attached to two linked CH groups (azirine cation). It is possible that the $m/z = 40$ ion has one of these two structures. We have given one of these structures in our Fig. 9. We assume that the cyclic structure is less probable for entropy reasons. Indeed, electron impact MS studies on imidazole show that the $m/z = 40$ cyclic azirine cation is produced by electron impact in the 17–26 eV range but not at lower energies [69]. It is therefore unlikely that the $m/z = 40$ ion produced in the onset region by photon impact is due to the cyclic ion azirine.

Finally, we remark that $C_3H_4^+$ can be eliminated as an assignment for $m/z = 40$, on thermochemical grounds (Table 3).

$m/z = 39$: This is a very weak ion, too weak for its AE to be measured. It is more likely to be C_2HN^+ (e.g. $HCCN^+$) than $C_3H_3^+$. Its formation could proceed by H-loss from $m/z = 40$, in which case we

estimate that the AE for this process is 13.6 + 2 eV = 15.8 eV, or it could be formed by H_2 loss from $m/z = 41$. The heat of formation of the $HCCN^+$ ion is $\Delta_f H(HCCN^+) = 15.87$ eV [29]. The single H atom loss channel, with our estimated AE, would give $\Delta_f H(C_2HN^+) = 11.26$ eV. However, if the estimated AE = 15.8 eV was similar for the H_2 loss channel from the $m/z = 41$ ion, the derived apparent $\Delta_f H = 15.78$ eV. This speculation leads to suggesting that the $m/z = 39$ ion is $HCCN^+$, formed by H_2 loss from the $m/z = 41$ ion.

$m/z = 28$: We have assigned this ion to a species with the elemental formula CH_2N^+. It is one of the most important fragment ions, and its AE = 11.34 ± 0.05 eV (Fig. 8) is in the Franck–Condon excitation gap. The inflexion rise in the fragment ion yield at about 13.2 eV is close to a sharp increase in the PES at 13.2 eV, where direct ionization occurs. Main-Bobo et al. report the AE = 11.67 ± 0.05 eV [28]. We note again that they used a many-line hydrogen source.

We first considered that this ion is formed by HCN + CH loss. From our AE we deduce an apparent $\Delta_f H(CH_2N^+) = 5.158$ eV. However, published values for $\Delta_f H(HCNH^+)$ are 9.751 eV [28], 9.627 eV [70], 9.813 eV [29] and ⩽9.974 eV [53], while $\Delta_f H(CNH_2^+)$ is listed as 11.49 eV [29]. These values are much above our apparent value $\Delta_f H(CH_2N^+) = 5.158$ eV. We note that $HCNH^+$ is the most stable isomer of H_2CN^+ [54,70].

We then envisaged that the neutral product is C_2H_2N and not HCN + CH. In this case our measured AE leads to the apparent $\Delta_f H(CH_2N^+) = 10.178 \pm 0.10$ eV, thus supporting the suggestion that C_2H_2N is the sole neutral product. The potential barrier is of the order of 400 meV. Indeed this channel, which involves breaking of the N3–C4 bond, is the one proposed in the dissociation scheme of Main-Bobo et al. [28]. The existence of a single component KER [28] is consistent with a single pathway to $m/z = 28$.

We remark that ring opening of $C_3H_4N_2^+$ should be more probable from a 4π radical cation formed by H shift, which has the diazadiene structure, than from the 5π radical cation, because an aromatic ring should require more energy for opening than the 2.68 eV internal energy available at the AE for the $m/z = 28$ ion. For example, in benzene, the fragment ions $C_4H_4^+$ and $C_3H_3^+$ have AE values that are 4.2 eV above the benzene IE [30]. A reasonable estimation of the loss of aromaticity in going from the 5π to the 4π radical cation of imidazole indicates that the 4π radical cation may be no more than 1 eV higher in energy than the 5π radical cation. Linear cation(s) resulting from ring opening, mentioned earlier, could be the common intermediate of the three fragmentation processes with AE in the range 11.34–11.41 eV (Table 3).

The alternative assignment of $m/z = 28$, the ethylene cation $C_2H_4^+$ can be discounted as involving a pathway that is too endothermic (Table 3).

The proposed principal fragmentation pathways in the VUV dissociative photoionization of imidazole are shown in Fig. 9.

3.4. Benzimidazole $C_7H_6N_2$

There are several tautomers possible for benzimidazole, corresponding to different positions of the two H atoms on the five-membered ring. In our gas phase studies only the 1H, 2H tautomer is expected [71,72]. The first few successive ionizations of benzimidazole are assigned as follows [23] (vertical IEs): 8.45 eV (π), 8.81 eV (π) 10.05 eV (σ_N), 10.79 eV (π), 11.38 eV (π). The principal ions in our 21 eV photon mass spectrum have m/z values 118, 91, 65, 64, 63, 52 and 41.

$m/z = 118$: The parent ion has a measured IE = 8.20 ± 0.05 eV (Fig. 10). The ion signal increases rapidly from 8.37 ± 0.01 eV, so that the region between 8.20 and 8.37 eV can be considered as a tail. We note that the first band in the PES of benzimidazole [22], which peaks at 8.44 eV, has a tail in this energy region, as does that
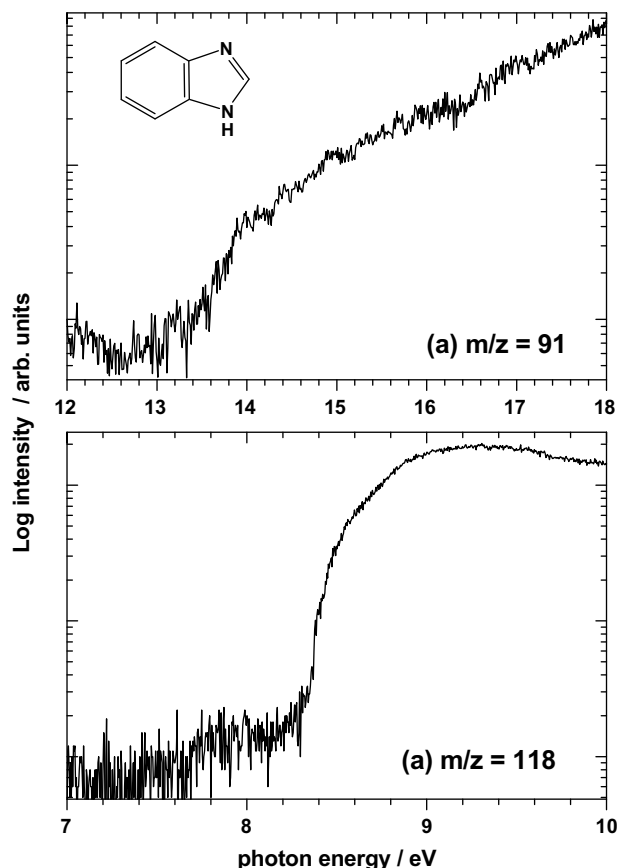
Fig. 10. Photoion yield curves of the benzimidazole parent cation and one of its fragment ions.

M.O. by Kovac et al. [23] as well as by Ramsey [22]. The parent ion yield curve also exhibits a fall off at 13.48 eV which is close to the onset of the HCN loss channel ($m/z = 91$) whose AE = 13.2 ± 0.2 eV, and is most probably related to the opening of this channel.

$m/z = 91$. This fragment ion is assigned to $C_6H_5N^+$, formed by loss of HCN from the parent ion. Its appearance energy is difficult to determine (Fig. 10) but is certainly greater than 12.8 eV. We consider a value 13.2 ± 0.2 eV as probable. This leads to a value for the enthalpy of formation $\Delta_f H(C_6H_5N^+) = 13.68 ± 0.22$ eV. There is a step in the $m/z = 91$ ion yield curve at 13.8 eV. This is close to the energy of the PES peak at 13.96 eV.

In benzimidazole the HCN loss channel occurs at 5.0 ± 0.2 eV above the ionization energy. This is much higher than HCN loss values in imidazole (2.75 eV), in purine or indeed in adenine. In these various species HCN is formed by bond breaking on the pentagon (as it must be in imidazole and benzimidazole) or on the hexagon as occurs in pyrimidine and is considered to be in adenine [5]. The presence of an aromatic benzo ring in benzimidazole, as compared with the ring containing two nitrogen atoms in purine and adenine might make it harder for bond breaking in the pentagon, in accordance with the decrease in mesomeric energy that ensues by substitution of carbon by nitrogen atoms.

An EI mass spectral study [74] has indicated that loss of HCN was preceded by rearrangement of the benzimidazole ion to the 2-amino-benzonitrile (*o*-cyanoaniline) ion. The latter molecule has a 70 eV EI mass spectrum practically identical to that of benzimidazole [30]. Two competitive reactions are thought to occur, involving elimination of HCN from the amino group and from the nitrile group, respectively. We have not represented these detailed stages in our Fig. 11. One could also propose 9-membered or 7-membered rings as intermediates but these would not be reasonable structures because of entropy arguments. Rearrangement of the parent ion to an ionized ylide (here an α-distonic ion in which there is an H-atom attached to each of the two nitrogen atoms) is improbable since the barrier to this interconversion is calculated to be 3.21 eV [75]. The rapid interconversion between benzimidazole and the ylide or to a common isomer has indeed been shown to be unlikely in studies by collision-induced dissociation and neutralisation–reionization mass spectrometry [75].

In another possible fragmentation scheme, not illustrated in Fig. 11, a linear $m/z = 118$ ion (1-aza-heptatriene radical cation) is formed by ring opening (i.e. opening of both rings, cleavage of bond C8–C9 and C2–N3 (see parent molecule, Fig. 11)), after which HCN is lost to form a set of *linear m/z = 91* ions which go on to dissociate to final products of lesser m/z (i.e. fragment ions $m/z = 65,64,52$ and 41). Heats of formation data are required to validate this scheme. We proposed an analogous scheme for the dissociative ionization of naphthalene and azulene in the "high energy" region (AE > 18 eV) [76].

$m/z = 65$. We have assigned this ion as $C_5H_5^+$, resulting from a concomitant loss of HCN + CN. The AE = 16.7 ± 0.15 eV. This fragment ion has an apparent $\Delta_f H = 12.67 ± 0.10$ eV. Five isomers of $C_5H_5^+$ are known either experimentally or on the basis of calculations [35,77]. In our case the $m/z = 65$ ion is most probably HC≡CCHCH=CH$_2^+$ (Pent-1-en-4-yn-3-yl radical ion) which has a reported $\Delta_f H = 11.73$ eV [29]. The other 4 isomers of $C_5H_5^+$ have the experimental or calculated $\Delta_f H$ values 10.487 eV vinylcyclopropenyl+, 10.902 eV cyclopentadienyl+, 12.0 eV an acyclic ion, and 11.865 eV a pyramidal ion.

$m/z = 64$: This ion is assigned as $C_5H_4^+$, resulting from the loss of 2HCN molecules from the parent ion. Its onset, AE > 16 eV, is difficult to determine. The apparent $\Delta_f H$ ($C_5H_4^+$) ⩽ 15.08 eV. This is greater than the reported [29] $\Delta_f H$ for the acyclic $C_5H_4^+$ species 1,2,3,4-pentatraene (13.66 eV), penta-1,4-diyne (14.64 eV), 1,3-pentadiyne (13.80 eV). If formed by H-loss from $C_5H_5^+$, the apparent
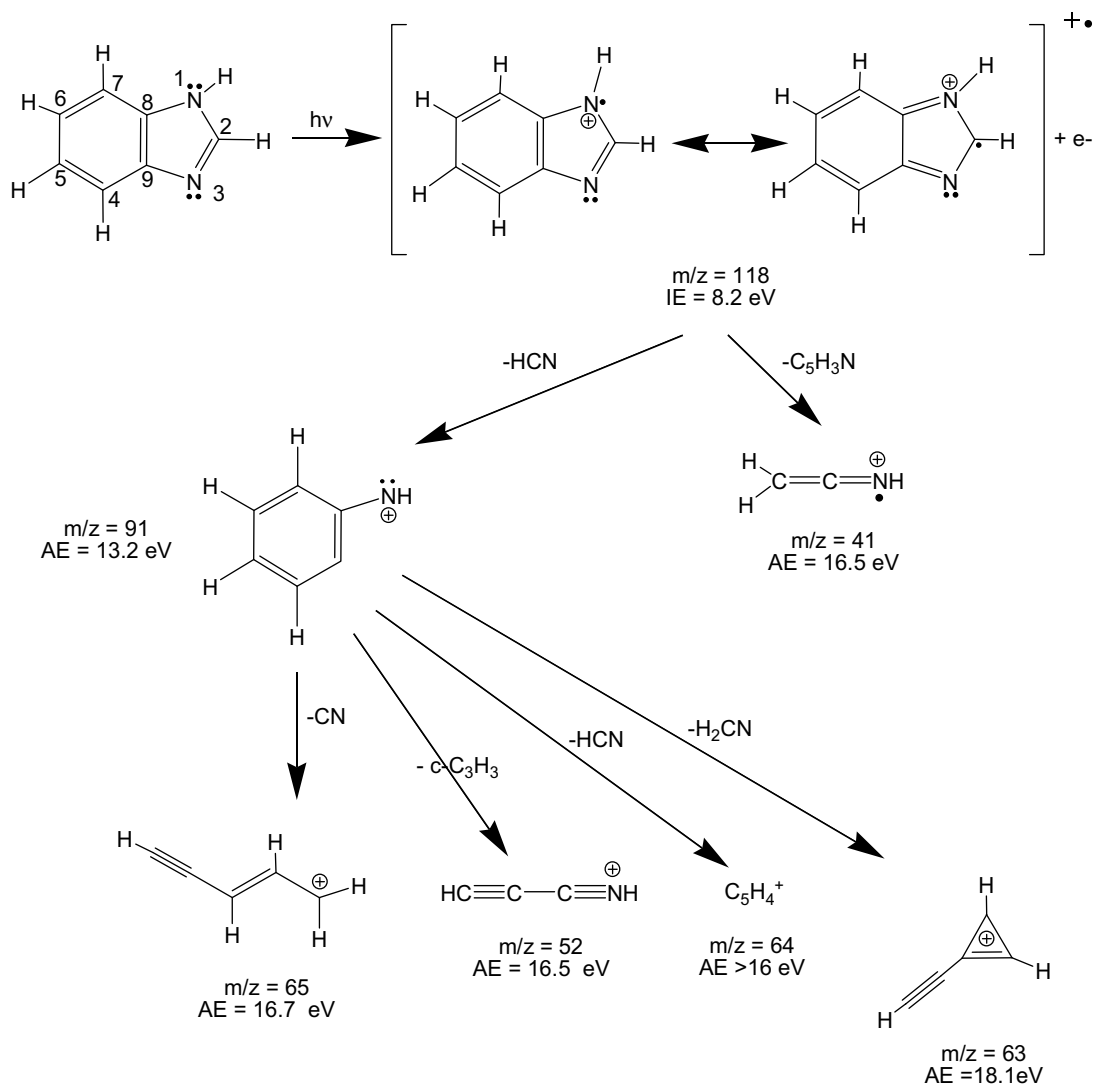
of Kovac et al. [23], who reported the peak to be at 8.45 eV. The NIST compilation [30] gives the adiabatic IE = 8.0 eV from the PES data of Ramsey [22] and of Kovac et al. [23], evidently from an estimation of the beginning of the tail in the PES band.

Our IE value is lower than the ionization energy, IE = 8.3754 ± 0.0006 eV, determined by R2PI and MATI measurements on jet-cooled benzimidazole [73]. Our experiments were carried out at a benzimidazole temperature $T = 130$ °C. At this temperature we estimate the internal energy for this large molecule to be about 90 meV, so that the "true" IE = 8.29 ± 0.05 eV, the upper limit of which is close to the value for cold benzimidazole. The difference between the adiabatic and vertical IEs is thus possibly no more than 80 meV. Ab initio calculations show that benzimidazole is planar in both the neutral and ion ground states [73]. Ionization therefore could induce excitation mainly of in-plane vibrations. However, the principal in-plane vibrations are relatively little modified in going from the neutral to the ion state [73], so that it is not surprising that the difference between adiabatic and vertical IEs is not very large in benzimidazole.

The enthalpy of formation of benzimidazole is $\Delta_f H(C_7H_6N_2) = 1.883 ± 0.014$ eV. Using our IE value, the enthalpy of formation of the benzimidazole ion is 10.173 ± 0.064 eV. A value $\Delta_f H(C_7H_6N_2^+) = 10.258 ± 0.015$ eV is obtained using the IE given by Lin et al. [58]. The Lias et al. value [29], based on IE(ad) = 8 eV (estimated onset of the photoelectron band), is 9.917 eV.

There are steps in the parent ion yield curve at (8.54), 8.96, 10.03, 10.50, 10.80, 11.27 eV: the 10.03 and 10.80 eV (perhaps also the 11.27 eV) steps coincide with PES peaks measured by Kovac et al. [23]. The 8.96 eV step is perhaps related to the 8.81 eV shoulder in the first PES band which, as noted above, is interpreted as a π

Fig. 11. Proposed principal fragmentation pathways in the VUV dissociative photoionization of benzimidazole.

$\Delta_f H$ would be much lower, $\geqslant 10.41$ eV. Thus the loss of 2 HCN molecules is the most likely reaction pathway.

$m/z = 63$: We assign this fragment ion to $C_5H_3^+$. The probable neutral loss products are HCN + H_2CN. The measured AE = 18.1 ± 0.1 eV. In calculating the enthalpy of formation of the fragment ion we used $\Delta_f H(H_2CN) = 2.3859 \pm 0.43$ eV (see section 3.3). With this value, we find $\Delta_f H(C_5H_3^+) = 16.192 \pm 0.53$ eV. This ion could be ethynylcyclopropropenylium ion, which is calculated to have $\Delta_f H = 16.3$ eV, and to be the most stable of 12 isomeric structures of $C_5H_3^+$ [78]. Another possible channel is loss of a H atom from $m/z = 64$. The corresponding apparent $\Delta_f H(C_5H_3^+) = 17.181$ eV.

$m/z = 52$: We made an initial provisional assignment of this ion to $C_4H_4^+$. The neutral fragment $C_3H_2N_2$ could be malononitrile. From the appearance energy of this ion, AE = 16.5 ± 0.2 eV, and assuming $C_4H_4^+$ + $C_3H_2N_2$ (malononitrile) as the dissociative ionization products, the apparent $\Delta_f H(C_4H_4^+) = 15.62 \pm 0.20$ eV. Known heats of formation of the various isomers of $C_4H_4^+$ are of the order of 12.6–12.9 eV [35], so that if our product assignments are correct, there are complex pathways to the products that involve energy barriers of the order of 2–3 eV.

Another possible assignment is to the $C_3H_2N^+$ ion with C_4H_4N as neutral product. No value has been reported for $\Delta_f H(C_4H_4N)$. The

$\Delta_f H(C_3H_2N^+)$ value in Willett and Baer [53] is $\leqslant 12.142$ eV. A value of $\Delta_f H = 11.684$ eV, from the proton affinity of HC≡CCN, is given by Lias et al. [29] for HCCCNH$^+$. If the neutral products were HCN + c-C_3H_3, this would lead to $\Delta_f H(C_3H_2N^+) = 12.422 \pm 0.38$ eV, in good agreement with the upper limit value of Willett and Baer. In our Fig. 11 we represent $m/z = 52$ as HC≡C–C≡N$^+$H.

$m/z = 41$: The two possible assignments of this ion are $C_2H_3N^+$ and CHN_2^+. In the first case, $m/z = 41$ could be CH_2CNH^+, as in imidazole, where other isomers, such as acetonitrile, were excluded. The concomitant neutral loss species is C_5H_3N. The second possible assignment, to CHN_2^+, involves the loss of C_6H_5 from the parent ion. This would involve rupture of the two aromatic C–N bonds and a H-shift to form the phenyl radical.

The measured AE = 16.5 ± 0.2 eV. Calculation of $\Delta_f H$ and comparison with literature values is not possible for both dissociation channels considered because $\Delta_f H$ values are unknown for C_5H_3N and for CHN_2^+. If $m/z = 41$ is the ketenimine ion CH_2CNH^+ its formation process does not proceed via formation of imidazole as the intermediate ion, since no $m/z = 68$ ion is observed for benzimidazole. Thus the nature of the $m/z = 41$ fragment ion is unknown. A further possible dissociation pathway could be to the CH_2CNH^+ ion and two neutral products, C_4H_2 and HCN. In this case we can

estimate $\Delta_f H(CH_2CNH^+) = 12.17 \pm 0.20$ eV, which is considerably greater than the enthalpy of formation of the ketenimine ion, $\Delta_f H = 10.41 \pm 0.04$ [53].

The proposed principal fragmentation pathways in the VUV dissociative photoionization of benzimidazole are given in Fig. 11.

4. Astrophysical implications

Nitrogen heterocyclic molecules are considered to be some of the possible building blocks of life [79]. If synthesized and preserved during the formation of the solar nebula, they could have been, and continue to be, transported to Earth via asteroids, comets and meteors, all of which vectors can provide protective environments. These molecules absorb strongly at 10.2 eV, where stellar emission of H Lyman-α is intense. Furthermore, in connection with the possible Earthbound delivery of biotic molecules from space, we note that the VUV luminosity of the early sun, during the Hadean period of considerable bombardment of the Earth from space, was more than two orders of magnitude higher than it is today, although the total luminosity was less [80]. Exploration of the VUV fragmentation behaviour of nucleic acid bases and related molecules is therefore of utmost importance in an exobiological context.

We first consider what could be the fate of the nitrogen heterocycles that we have studied if they were formed in the *interstellar medium* (ISM). The ionization energies are respectively 9.21 eV (pyrimidine), 9.35 eV (purine), 8.66 eV (imidazole) and 8.20 eV (benzimidazole). A rule of thumb [81] indicates that for a number of aromatic molecules of similar size to those studied here, the quantum yield of photoionization increases roughly linearly from the ionization onset and reached unity at about 9.2 eV above this onset energy. In HI regions in space, the upper energy limit of UV radiation is 13.6 eV. Thus, in these regions, the maximum ionization yields would be expected to be in order of magnitude: pyrimidine 48%, purine 46%, imidazole 54%, benzimidazole 59%. From our PIMS results, the lowest energy thresholds for dissociative ionization are: pyrimidine ($\geqslant 11$ eV), 12.27 eV; purine 12.6 eV, imidazole 11.34 eV, benzimidazole 13.2 eV. Thus, the four species studied could undergo dissociative ionization in HI regions, but with relatively small yields for purine and especially benzimidazole, whose dissociative ionization thresholds are 1 eV or less below 13.6 eV.

We note that a study of the lifetime of pyrimidine under UV photolysis, related to its survival in space, has been made by Peeters et al. [82]. They irradiated an argon matrix containing pyrimidine at 12 K with a hydrogen lamp emitting UV photons with a flux of 4.6×10^{14} photons $cm^{-2} s^{-1}$. From a measure of the rate of disappearance of the pyrimidine I.R. absorption under these conditions, they estimated the photodestruction cross section of pyrimidine (1.2×10^{-17} cm^2 molecule^{-1}), as well as the half-life, 8.1 yr, in the diffuse interstellar medium, and 0.81 Myr in dense interstellar clouds. These estimated values relate to integrated

photolysis effects only up to Lyman-α 10.2 eV since there is relatively little emission above this energy by a microwave-excited hydrogen flow source, apart from the question of window transmission (not detailed). Thus in the work of Peeters et al. no account is taken of the effects of VUV radiation above 10.2 eV. At this limiting energy, which is below the pyrimidine dissociative ionization energy, we estimate the ionization yield (in the gas phase) to be only 11%. We remark that the destruction rates and half-lives determined by Peeters et al. are certainly dependent on solid state effects and on the chemical nature of the matrix [83]. It is thus somewhat illusory to extrapolate these rates to the gas phase relevant in interstellar sites.

Laboratory work has suggested that purines and pyrimidines might be formed in the ISM starting from hydrogen cyanide or cyanoacetylene [79], or from even more simple gases like NH_3, N_2, CO_2 and H_2O [84]. Speculation has been made on the possible formation of adenine in the ISM by successive condensation reactions of HCN [85] but this proposal has been contested by Smith et al. [86]. A very recent computational study of mechanisms of prebiotic pyrimidine-ring formation of monocyclic HCN-pentamers, with application to adenine synthesis is space, has been carried out by Glaser et al. [87]. Observation of pyrimidine and imidazole in the interstellar medium (ISM) by radioastronomy has been attempted but has not been successful so far. Upper limits of abundance have been established for pyrimidine [88] and imidazole [89]. More recently, a particular interstellar spectral feature, previously observed in hot molecular cores towards W51 e1/e2 [88], is considered as being possibly due to pyrimidine, and has been re-analyzed favorably [90], but this is insufficient to confirm the pyrimidine assignment without justification via other lines, possibly due to pyrimidine, which require further observation and study. A search for pyrimidine in circumstellar envelopes of carbon-rich stars, thought to be a suitable site for pyrimidine observation, was unsuccessful [88].

Protection from the destructive effects of VUV radiation is necessary for detectable amounts of these nitrogen heterocyclic molecules to exist in the ISM. Observations should be fruitful towards protostars [91,92], in particular in hot molecular cores [93], which are warm condensations inside molecular clouds associated with active star formation regions, whose density is such that they will offer molecules some protection against radiation. Another interesting site to consider is the planet formation region of young circumstellar disks. It has been found that the abundances of simple organic molecules and water for AA Tauri, a typical young star with an accretion disk, are about one order of magnitude higher than for observed molecular cores [94], indicating that molecular synthesis takes place within the disk. We suggest that in further attempts to observe these species, as well as nucleobases such as adenine, a suitable tracer could be the HCN molecule, the principal neutral fragment of dissociative ionization of these molecules, and a well observed species in hot cores in the ISM [95] as well as being a species with a relatively high abundance in AA Tauri. The disso-

Table 2
Purine ($C_5H_4N_4$) appearance energy measurements and possible fragmentation products

m/z	AE/eV	Fragment cation m_1^+	Neutral fragments *process assignments in bold*	Apparent $\Delta_f H_{gas}(m_1^+)$/eV	Literature value $\Delta_f H_{gas}(m_1^+)$/eV *Ion assignments in bold*
120 (Parent ion)	9.35 ± 0.05 (IE)			11.733 ± 0.05	**$C_5H_4N_4^+$**: ⩽11.91
93	12.6 ± 0.05	$C_4H_3N_3^+$	**HCN**	13.58 ± 0.08	**$C_4H_3N_3^+$**:[b]
		$C_3HN_4^+$	C_2H_3	11.88 ± 0.13	$C_3HN_4^+$:[b]
66	13.24 ± 0.1	$C_3H_2N_2^+$	**2HCN**	12.82 ± 0.13	**$C_3H_2N_2^+$**: (15.56 ± 0.1[a]; 12.56; 11.56; 11.20: see text)
		$C_2N_3^+$	HCN + C_2H_3	11.12 ± 0.18	$C_2N_3^+$:[b]

Apparent enthalpies of formation have been calculated using values listed in Table 5.
[a] Malononitrile cation.
[b] Standard enthalpy of formation is not available in the gas phase from the NIST standard reference data base.

ciative photoionization threshold energies for the ejection of HCN are: pyrimidine 12.27 eV, purine 12.6 eV, imidazole 11.41 eV, benzimidazole 13.2 eV (Tables 1–4), adenine 11.56 eV [5]. In the same spirit, we remark that HNCO would be a suitable tracer for thymine and for uracil [5]. Although pyrimidine is a precursor of thymine and uracil, the presence of O atoms in these nucleobases gives rise to important dissociative ionization channels involving loss of HNCO rather than HCN. HNCO has also been observed in hot cores in the ISM by radioastronomy [95,96].

Turning to the *solar system*, we note that pyrimidines and purines have been reported in the data obtained with the PUMA dust impact mass spectrometer during the flyby of comet Halley by the Soviet spacecraft VEGA 1 [97]. However, the mass resolution was insufficient to specify particular species in these molecular categories. The organic gas composition was measured aboard the GIOTTO spacecraft by the PICCA ion mass spectrometer which measured ions in the $m/z = 10$–210 range with an effective mass resolution, outside the ionopause, of about 3 Da. Combining the results with other observations led to the conclusion that the molecular gas phase ions observed, which include relatively small ions containing nitrogen, are derived from larger polymers present in the cometary matter [98]. More recently, pyrolysis-GC–MS has been applied to analyse HCN-polymers which may be among the organic macromolecules most readily formed within the solar system [99]. These polymers can form spontaneously from HCN in the presence of trace quantities of base catalysts. The resulting black solid, analyzed by Minard et al. [99], contains the purine based nucleic acid bases adenine and xanthine (as methylated derivatives), and other nitrogen heterocyclic molecules. Prebiotic synthesis of adenine has been achieved by Levy et al. under Europa-like conditions in a study of dilute solutions of NH_4CN frozen for 25 years at low temperatures [100]. Kobayashi and Tsuji have shown that that the nucleobase uracil can be formed from a simulated primitive atmosphere of CO, N_2 and H_2O irradiated by protons [101]. Purine based nucleic acid bases, as well as certain hydroxyl-pyrimidines, have been found in the formic acid extract of carbonaceous chondrites [102,103]. Indeed, Schwartz has stated categorically that purines and smaller amounts of pyrimidines, have been identified in meteorites [104], as was claimed earlier, more cautiously, by Cronin et al. [105]. This has very recently been verified by the identification of a pyrimidine, uracil, and a purine, xanthine, in the Murchison meteorite [106]. These compounds have carbon isotope ratios which are consistant with their non-terrestrial origin. Our results show that naked exposure to the VUV radiation emitted by the sun could lead to dissociative photoionization of purines and pyrimidines at energies greater than about 11 eV (wavelengths

Table 3
Imidazole ($C_3H_4N_2$) appearance energy measurements and possible fragmentation products

m/z	AE/eV	Fragment cation m_1^+	Neutral fragments *process assignments in bold*	Apparent $\Delta_f H_{gas}(m_1^+)$/eV	Literature value $\Delta_f H_{gas}(m_1^+)$/eV *Ion assignments in bold*
68 (Parent ion)	8.66 ± 0.03 (IE)			10.04 ± 0.03	$C_3H_4N_2^+$: 10.31 (see text)
67	11.38 ± 0.05	$C_3H_3N_2^+$	**H**	10.56 ± 0.06	$C_3H_3N_2^+$: 10.99
	12.05 ± 0.03(see text)			(11.17 ± 0.04, see text)	
41	11.41 ± 0.05	$C_2H_3N^+$	**HCN**	11.39 ± 0.06	CH_2CNH^+:10.41 ± 0.04; 12.97[c]; 12.9[d]; see text
		CHN_2^+	C_2H_3	9.69 ± 0.11	[b]
40	13.83 ± 0.05	$C_2H_2N^+$	**HCN + H**	11.55 ± 0.06	$C_2H_2N^+$: 12.58; 12.82 ± 0.43 (see text)
		$C_3H_4^+$	N_2	15.21 ± 0.06	$C_3H_4^+$: 12.28[e]
39	[a]	C_2HN^+	**HCN + H$_2$**		$HCCN^+$: 15.87
		$C_3H_3^+$	N_2H		
28	11.34 ± 0.05	CH_2N^+	HCN + CH	5.158 ± 0.05	$HCNH^+$: 9.813
			CH$_2$CN	10.178 ± 0.10	
		$C_2H_4^+$	CNN, NCN	6.66 ± 0.05	$C_2H_4^+$: 11.059 ± 0.008
				7.82 ± 0.05	

Apparent enthalpies of formation have been calculated using Table 5.
[a] Very weak ion, AE measurement difficult or not possible.
[b] Standard enthalpy of formation is not available in the gas phase from the NIST data base.
[c] Aacetonitrile cation.
[d] Methylisocyanide cation.
[e] Propyne cation.

Table 4
Benzimidazole ($C_7H_6N_2$) appearance energy measurements and possible fragmentation products

m/z	AE/eV	Fragment cation m_1^+	Neutral fragments *process assignments in bold*[a]	Apparent $\Delta_f H_{gas}(m_1^+)$/eV	Literature value $\Delta_f H_{gas}(m_1^+)$/eV *ion assignments in bold*[a]
118 (Parent ion)	8.20 ± 0.05 (IE, see text)			10.173 ± 0.064 (see text)	$C_7H_6N_2^+$: 9.917 (based on IE = 8.0 eV, see text)
91	13.2 ± 0.2	$C_6H_5N^+$	**HCN**	13.68 ± 0.22	$C_6H_5N^+$:[b]
65	16.7 ± 0.1	$C_5H_5^+$	**HCN + CN**	12.67 ± 0.10	$HC{\equiv}CCHCH{=}CH_2^+$: 11.73
64	>16	$C_5H_4^+$	**2HCN**	⩾15.08	**Isomers $C_5H_4^+$0**: 13.66; 14.64; 13.80
			HCN + CN + H	⩾10.41	(acyclic isomers, see text)
63	18.1 ± 0.1	$C_5H_3^+$	**HCN + H$_2$CN**	16.19 ± 0.53	$C_5H_3^+$: ⩾16.3[c] (see text)
			2HCN + H	17.181	
52	16.5 ± 0.2	$C_4H_4^+$	**C$_3$H$_2$N$_2$**	15.62 ± 0.2	$C_4H_4^+$: 12.6–12.9 (see text)
		$C_3H_2N^+$	**HCN + c-C$_3$H$_3$**	12.42 ± 0.38	$C_3H_2N^+$: ⩽12.14
41	16.5 ± 0.2	$C_2H_3N^+$	C_5H_3N		CH_2CNH^+: 10.41 ± 0.04
			C_4H_2 + HCN	12.17 ± 0.20	
		CHN_2^+	C_6H_5		CHN_2^+:[b]

Apparent enthalpies of formation have been calculated using values listed in Table 5.
[a] Two ion assignments are possible for $m/z = 52$ and for $m/z = 41$, shown in bold. The corresponding neutral products for $m/z = 41$ are not shown in bold, due to lack of sufficient ΔH data (see text).
[b] Standard gas phase enthalpy of formation is not available in the NIST reference data base [30].
[c] Ethynylcyclopropenylium cation, calculated value.

Table 5
Gas phase standard enthalpies of formation used for thermochemical calculations[a]

Species	$\Delta_f H_{gas}$/eV
Pyrimidine	2.029 ± 0.015
Purine	2.383[b]
Imidazole	1.377 ± 0.006
Benzimidazole	1.883 ± 0.015
H	2.259
HN_2	2.93 ± 0.05
CH	6.158[c]
C_2H (ethynyl radical)	4.944[c]
C_2H_2	2.350[c]
$C_2H_2^+$	13.750[d]
C_2H_3 (vinyl radical)	3.10 ± 0.05
$C_2H_3^+$	11.4 ± 0.1
C_2H_4 (ethylene)	0.544[c]
$C_2H_4^+$ (ethylene cation)	11.059 ± 0.008
c-C_3H_3	4.56 ± 0.18
C_3H_4 (propyne, cyclopropene)	1.922 ± 0.008; 2.87 ± 0.05
$C_3H_4^+$ (propyne cation, cyclopropene cation)	12.28 ± 0.02[d]; 12.54 ± 0.06
C_4H_2 (Diacetylene)	4.808 (Uncertainty not indicated)
C_4H_4 (1-Buten-3-yne)	3.057 (Uncertainty not indicated)
$C_4H_4^+$ (1-Buten-3-yne cation)	12.64 ± 0.02[d]
CN	4.510[c]
CN^+	18.14 ± 0.05
CNN radical, NCN radical	6.058[c]; 4.900[c]
C_2N_2 (dicyanogen)	3.203[c]
$C_2N_2^+$ (Dicyanogen cation)	16.573 ± 0.01[d]
HCN (hydrogen cyanide)	1.401[c]
HCN^+ (hydrogen cyanide cation)	15.00 ± 0.01[d]
H_2CN	2.39 ± 0.43[e]
C_2H_2N (CH_2CN)	2.54 ± 0.10
C_2H_3N (acetonitrile, methylisocyanide)	0.767 ± 0.004; 1.69 ± 0.08
C_2H_3N (acetonitrile cation, methylisocyanide cation)	12.97 ± 0.01[d]; 12.93 ± 0.1
C_3H_3N (2-propenenitrile)	1.862 (Uncertainty not indicated)
$C_3H_3N^+$ (2-propenenitrile cation)	12.77 ± 0.01[d]
$C_3H_2N_2$ (malononitrile)	2.76 ± 0.01
$C_3H_2N_2^+$ (malononitrile cation)	15.56 ± 0.1[d]

[a] Data from NIST [30]. The experimental uncertainty is not indicated in cases where it is below 0.001 eV.
[b] Estimated value in Lias et al. [29].
[c] Originally from Chase, 1998.
[d] $\Delta_f H_{gas}$(cation) = $\Delta_f H_{gas}$(neutral molecule) + IE.
[e] See text.

less than 112.7 nm). The flux of solar radiation in this spectral region was much higher in the early life of the Sun than it is today, with perhaps as much as 10^4 times more UV radiation below 200 nm [107]. Thus protection provided by encapsulation of these prebiotic molecules in meteors, asteroids and comet nuclei is required for their survival in the solar system, whether they are formed early or late in the life of the Sun, before eventually reaching the Earth.

5. Conclusion

Our photoionization mass spectrometry (PIMS) study of pyrimidine and purine, and of the related molecules imidazole and benzimidazole has astrobiological interest since these molecules are possible precursors of the nucleobases present in DNA and RNA. Knowledge of their response to and behaviour under VUV irradiation is necessary for evaluating their capacity to be formed and survive in various astrophysical media as well as for proposing sites for their observation in space. The photoion yield curves of parent and fragment ions of the four species under study were measured as a function of incident photon energy in the 7–18 eV range, using monochromatised synchrotron radiation as excitation source. Features and steps in the ion yield curves are discussed in relation to the nature and energies of specific ionization processes. The measured adiabatic ionization energies of purine and imidazole are reported for the first time, whereas the values for pyrimidine and

benzimidazole are improved or confirmed. Differences in the adiabatic and vertical ionization energies for pyrimidine are of the order of 500 meV, in agreement with calculations reflecting nuclear reorganization energies on ionization. The corresponding measured differences for purine ($\approx$260 meV), imidazole ($\approx$150 meV) and benzimidazole ($\leqslant$80 meV) are smaller. These differences represent test values for calculations which are called for on the adiabatic and vertical ionization energies of these molecules.

Many of the fragment appearance energies were previously unknown or, if reported, were of restricted precision. The previously available data are mainly from electron impact measurements. Our detailed exploration of dissociative photoionization pathways is based in part on thermochemical grounds, involving the determination of enthalpies of formation for various dissociation channels, which has led to the choice of specific ionic and neutral products and to discrimination between alternative dissociation processes. The possible role of ylide structures of the parent cation is considered in some cases. H-loss from the parent ion is either weak (pyrimidine, imidazole) or absent (purine, benzimidazole), while H_2 loss from the parent ion is not observed. These observations are in marked contrast to the fragmentation behaviour of the species isoelectronic with pyrimidine, benzene, which exhibits H and H_2 loss from the cation as important low energy processes. In the case of the azines, the ionization is from a heteroatom whereas in benzene, ionization is of a π electron in an all carbon system.

The major dissociation channels in these four species involve single or multiple loss of HCN, as is the case also of the nucleobase adenine, which is closely related to purine. Loss of a single HCN molecule requires significantly less internal energy in the imidazole cation (2.75 ± 0.08 eV) than for purine, pyrimidine or adenine (3.2–3.4 eV), and very much less than for benzimidazole (5.0 ± 0.2 eV). Quantum chemical calculations on the structure and stability of the fragment cation resulting from HCN loss would be useful in order to rationalise these observations in each case and to confirm the assignment of the dissociation products. There are also notable differences, among the four species studied, concerning the internal energy in the cation required to expel two HCN molecules. Indeed, this process is not observed for imidazole, where the resulting cation would be the methylene ion. Here again, quantum chemical calculations of the proposed fragmentation channels are required. It is of interest that the presence of a NH_2 group in adenine, with respect to purine, does not hinder the HCN loss channel. However, the presence of an oxo group in the nucleobase guanine, which is a related purine and which also possesses a NH_2 group, modifies profoundly the dissociative ionization processes, since HCN and 2HCN loss processes are not observed for this species [108].

After a detailed discussion of the assignments of the dissociation products and proposed fragmentation processes of the four species under study, we consider the astrophysical implications of our results. Using a previously determined rule of thumb for estimating the behaviour of the quantum yield of photoionization as a function of incident photon energy, assessment is made of the degree of photoionization under VUV excitation in the gas phase, notamment in the HI regions of the interstellar medium. Effects of the solid phase on destruction and ionization yields are also discussed. Proposals are made of suitable interstellar sites for radioastronomical observation of nucleobases or their precursor molecules, helped via suggested tracer molecules. Finally, some discussion is given concerning Solar system observations of pyrimidines and purines in cometary and meteoritic media and the necessity of their encapsulation for survival during transfer through space to the Earth, both at the present time and during the early life of the Sun when the flux of VUV radiation was much higher.

Acknowledgements

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