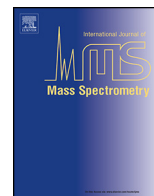




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Multi-photon and electron impact ionisation studies of reactivity in adenine–water clusters

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ABSTRACT

Multi-photon ionisation (MPI) and electron impact ionisation (EII) mass spectrometry experiments have been carried out to probe unimolecular and intermolecular reactivities in hydrated adenine clusters. The effects of clustering with water on fragment ion production from adenine have been studied for the first time. While the observation of NH_4^+ fragments indicated the dissociation of protonated adenine, the dominant hydration effects were enhanced $\text{C}_4\text{H}_4\text{N}_4^+$ production and the suppression of dissociative ionisation pathways with high activation energies. These observations can be attributed to energy removal from the excited adenine radical cation via cluster dissociation. Comparisons of MPI and EII measurements provided the first experimental evidence supporting hypoxanthine formation in adenine–water clusters via theoretically predicted barrierless deamination reactions in closed shell complexes.

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1. Introduction

Radiation induced processes in DNA bases have been investigated intensively in recent years in order to better understand the fundamental process that can initiate DNA lesions [1]. Further interest relates to the mechanisms underpinning the remarkable photo-stability of DNA bases and their possible evolutionary implications. While studies of isolated molecules generally provide the clearest data interpretations, equivalent experiments on hydrogen-bonded complexes enable closer analogies to be drawn with biological environments where different isomeric forms, intermolecular energy transfer processes, and reactivity can be significant. The relaxation pathways of both isolated and hydrated adenine ($\text{C}_5\text{H}_5\text{N}_5$) following excitation to the lowest lying bright $\pi\pi^*$ state have been mapped out in considerable detail using ultrafast pump-probe experiments [2–4] and quantum chemical

calculations [5–7]. Sub-ps-timescale internal conversion to the vibrationally hot electronic ground state via intermediary $n\pi^*$ and $\sigma\pi^*$ states is found to dominate, although evidence for much weaker intersystem crossing pathways to long-lived triplet states has also been reported [8]. Previous studies of reactivity in hydrated adenine have focused on tautomeric transitions [9,10] and proton transfer in adenine dimer ions [11]. However, no experiments have directly explored the effects of hydration on the dissociative ionisation pathways of adenine. The present work applies UV multi-photon ionisation (MPI) mass spectrometry to analyse fragment ion production from adenine–water clusters. Furthermore, we have carried out the most detailed analysis to date of MPI and electron impact ionisation (EII) production of hydrated adenine monomer ions and hydrated reaction products (notably hydrated protonated adenine) from larger dissociated clusters. The key interest in directly comparing MPI and EII of mixed clusters stems from the selective nature of MPI, notably with water molecule photo-excitation being inaccessible in the present laser conditions.

One possible reaction product of adenine and water that would not be readily identifiable in the mass spectra of hydrated adenine

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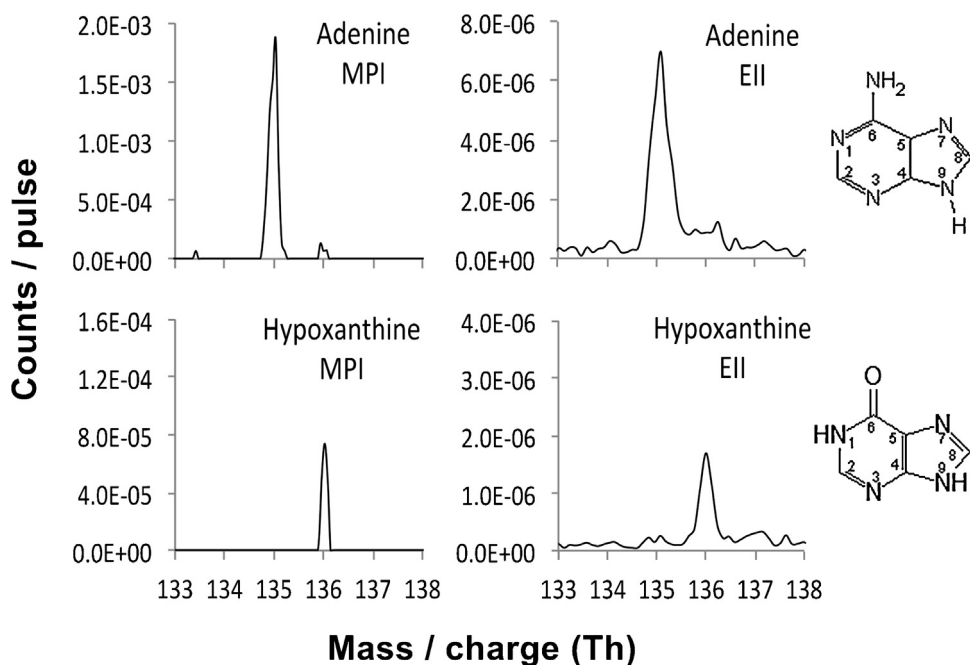


Fig. 1. Comparison of MPI (220 nm, average fluence $4 \times 10^7 \text{ W cm}^{-2}$) and EII (200 eV) of adenine and hypoxanthine (Ar 0.5 bar). The most abundant gas-phase tautomers (amine-N9H adenine [19] and keto-N1H/N9H hypoxanthine [20]) are shown on the right.

is hypoxanthine ($\text{C}_5\text{H}_4\text{N}_4\text{O}$) with mass 136 a.u., equal to protonated adenine or an adenine isotopomer containing one ^{13}C . The most abundant gas-phase tautomers of adenine (amine-N9H [19]) and hypoxanthine (keto-N1H/N9H [20]) are shown schematically in Fig. 1. A negative activation barrier for hypoxanthine production in the closing system of four water molecules around adenine has been predicted theoretically [12,13]. While the aim of the present MPI and EII experiments on hypoxanthine is to elucidate adenine–water reactivity, the molecule is also interesting as a *universal* nucleobase that binds without discrimination to natural bases. Its potential applications in polymerase chain reaction (PCR) hybridisation probes and gene therapies have been discussed by Rutledge et al. [14]. In contrast with adenine, very few experimental studies of the photophysical properties of hypoxanthine have been reported in the literature. Electronic spectra and excited state geometries have been investigated theoretically [15], both in isolated and hydrated conditions. As with DNA bases, $\pi\pi^*$ transitions dominate hypoxanthine absorption in the wavelength range (220–225 nm, 5.64–5.51 eV) of the present MPI experiments. Further studies have been focused on hydrogen bonding and stacking interactions with DNA bases [14] and gas phase acidity and proton affinity [16].

2. Experimental

The experimental system has been described in a recent publication [17]. Briefly, argon seeded with sublimated adenine or hypoxanthine (Sigma–Aldrich, minimum purity 99%) with or without water vapour flowed continuously through a pin-hole (70 μm diameter in Fig. 1, 50 μm in Figs. 2 and 3) into a pumped chamber to form a supersonic jet. The argon pressure was varied between 0.5 and 1.8 bar in order to modify the level of clustering in the neutral beam. The highly stable adenine–water clustering conditions required to directly compare MPI and EII mass spectra were achieved by controlling the water and nozzle temperature to within $\pm 1^\circ\text{C}$ using continuous resistive heaters and keeping all parts of the gas line at higher temperatures than the water reservoir. The adenine temperatures (237–276 $^\circ\text{C}$) were

comparable with or lower than those applied in previous supersonic beam experiments that reported no evidence for thermally driven decomposition, isomerisation, or reactivity of adenine [18]. The jet passed through a skimmer into a second pumped chamber and crossed an Nd:YAG pumped dye laser beam (*Continuum Powerlight II 8000 – Sirah Cobra-Stretch*, repetition rate 10 Hz, pulse width 7 ns, pulse energy 100–2000 μJ , wavelength 220–277 nm) for MPI measurements or a 200 eV electron beam generated by a commercial gun (*Kimball ELG-2*) for EII experiments. The resulting ions were detected using a reflectron time-of-flight (TOF) mass spectrometer (KORE Technology). The pre-amplified ion signals were timed using a 250 ps resolution *Fast Comtec P7887* time-to-digital conversion (TDC) card. The highest mass resolution we have attained to date was $m/\Delta m = 2000$ using a focused laser beam. The data acquisition system was based on a *LabView* application interfacing with the TDC card and a laser pulse energy meter (*Spectrum Detector SPJ-D-8*). A convex lens on a slider was used to control the laser spot diameter at the interaction with the molecular beam and the average laser pulse energy was adjusted

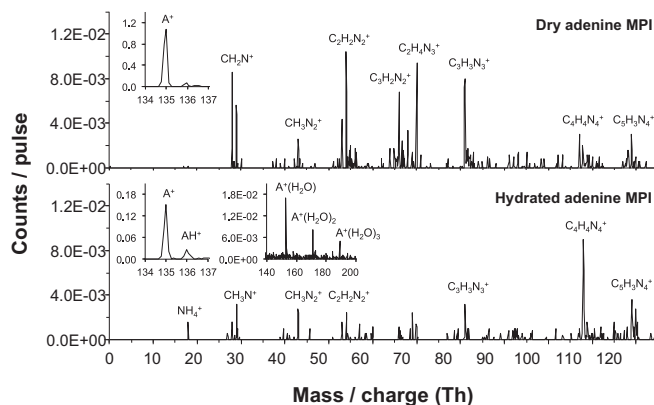


Fig. 2. MPI mass spectra (225 nm, average fluence $4 \times 10^5 \text{ W cm}^{-2}$, powder 237 $^\circ\text{C}$, Ar 0.8 bar) of dry adenine and hydrated adenine (water 100 $^\circ\text{C}$).

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