

## Dissociative multi-photon ionization of isolated uracil and uracil-adenine complexes



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### ABSTRACT

Recent multi-photon ionization (MPI) experiments on uracil revealed a fragment ion at  $m/z$  84 that was proposed as a potential marker for ring opening in the electronically excited neutral molecule. The present MPI measurements on deuterated uracil identify the fragment as  $C_3H_4N_2O^+$  (uracil<sup>+</sup> less CO), a plausible dissociative ionization product from the theoretically predicted open-ring isomer. Equivalent measurements on thymine do not reveal an analogous CO loss channel, suggesting greater stability of the excited DNA base. MPI and electron impact ionization experiments have been carried out on uracil-adenine clusters in order to better understand the radiation response of uracil within RNA. Evidence for  $C_3H_4N_2O^+$  production from multi-photon-ionized uracil-adenine clusters is tentatively attributed to a significant population of  $\pi$ -stacked configurations in the neutral beam.

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### 1. Introduction

The dynamics and stabilities of nucleobases following excitation to their bright  $S_2(\pi\pi^*)$  states have been researched intensively in recent years [1]. Time resolved pump-probe experiments [2] and calculations [3] on isolated molecules have yielded rich insights into their excited state dynamics, while studies of base pairs and hydrated clusters have enabled closer analogies to be drawn with cellular environments [4]. Internal conversion to the vibrationally hot electronic ground state (either directly or via  $S_1$  states of mainly  $n\pi^*$  and  $\sigma\pi^*$  character) dominates  $S_2(\pi\pi^*)$  deactivation [5,6], although intersystem crossing to long-lived triplet states has also been identified [7,8]. The present work investigates dissociative multi-photon ionization (MPI) of uracil ( $C_4H_4N_2O_2$ ) as a tool to gain additional understanding of its relaxation pathways from  $S_2(\pi\pi^*)$  and from excited ionic states. Uracil forms two hydrogen bonds with adenine in RNA and is geometrically similar to the DNA base thymine ( $C_5H_6N_2O_2$ ; uracil methylated at the C5 site of the pyrimidine ring system).

Structural modifications and bond breaking in electronically excited or ionized DNA and RNA bases are of particular interest as they represent potential radiation damage pathways in the respective macromolecules. Nachtigallová et al. [9] theoretically identified ring-opening at the  $S_2(\pi\pi^*)$ - $S_1(\sigma(n-\pi)\pi^*)$  crossing seam. More recently, Richter et al. [10] carried out dynamical calculations with non-adiabatic and spin-orbit couplings that supported this pathway. The ring-opening process was predicted to lead to new photochemical products [9]. Barc et al. [11] observed a new fragment ion at  $m/z$  84 (uracil<sup>+</sup> minus CO or  $CNH_2$ ) by single-color 2-photon ionization of uracil. The threshold photon energy ( $5.29 \pm 0.06$  eV) for this product agreed with the calculated energy (5.25 eV at CASSCF level) of the ring-opening crossing seam [9] and the geometry of the predicted isomer indicates likely CO abstraction. Therefore MPI production of this fragment ion was proposed as a potential experimental marker for ring opening in neutral excited uracil, suggesting possibilities for diverse measurements exploring the process in depth (e.g. using coincidence and/or time-resolved methods). The first aim of the present work was to test if the new fragment ion is indeed due to CO loss by studying MPI of deuterated uracil (dominantly  $C_4D_4N_2O_2$ ). These results have the added value of identifying several previously debated fragments from the radical cation, while further evidence to assign specific peaks is provided by high-resolution MPI mass spectra. The paper

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also presents equivalent MPI measurements on thymine, for which no analogous ring-opening process has been predicted [9]. A distinctly higher pump energy (5.64 eV, 220 nm) was applied than in the previous MPI studies of thymine (4.34–4.77 eV, 285.7–260 nm) [6,12–17], increasing the likelihood of isomeric transitions during radiationless deactivation. Finally, MPI and electron impact ionization (EII) experiments were carried out on uracil-adenine clusters as a step towards better understanding the dissociative ionization pathways of uracil within RNA. Whereas several spectroscopic studies have been carried out on adenine-thymine complexes in supersonic beams [18–20], to our knowledge no previous experiments on isolated uracil-adenine clusters have been reported in the literature.

## 2. Experimental

The experimental system has been described in detail by Barc et al. [11]. Briefly, argon or helium carrier gas (0.5–1.2 bar) seeded with sublimated uracil, thymine, adenine (all Sigma-Aldrich with stated purity  $\geq 99\%$ ) and/or deuterated uracil (*uracil-d4*, CDN isotopes, 98.4%) flowed continuously through a 50  $\mu\text{m}$  diameter pinhole into a pumped chamber ( $500\text{ l s}^{-1}$  in the measurements shown in Figs. 1–4;  $1000\text{ l s}^{-1}$  in Fig. 5) to form a supersonic jet. The powder temperatures (250–277 °C) were comparable with or lower than those applied in previous mass spectrometry and IR spectroscopy experiments that reported no evidence for thermally driven decomposition, isomerization, tautomerization, or reactivity in uracil, adenine, or thymine following sublimation in inert gas [21]. The carrier gas pressure, the powder temperature, and the pumping speed in the expansion chamber were modified in order to gain control over the level of clustering in the jet. However the greatest effect was achieved by changing the carrier gas; the experiments in helium expansions showed no evidence for clustering. The jet passed through a skimmer into a second pumped chamber and crossed an Nd:YAG pumped and frequency doubled dye laser beam (*Continuum Powerlight II 8000 – Sirah Cobra-Stretch*, repetition rate 10 Hz, pulse width 7 ns, pulse energy 100–2000  $\mu\text{J}$ , wavelength 219–277 nm). A commercial electron gun (*Kimball ELG-2*) provided an alternative ionizing beam. The resulting ions were detected using a reflectron time-of-flight (TOF) mass spectrometer (supplied by KORE Technology and shown schematically in Fig. 1a) with the *field free region* held at  $-2\text{ kV}$ . The pre-amplified ion signals were timed using a *Fast Comtec P7887* time-to-digital conversion (TDC) card with a minimum bin size of 250 ps. The data acquisition

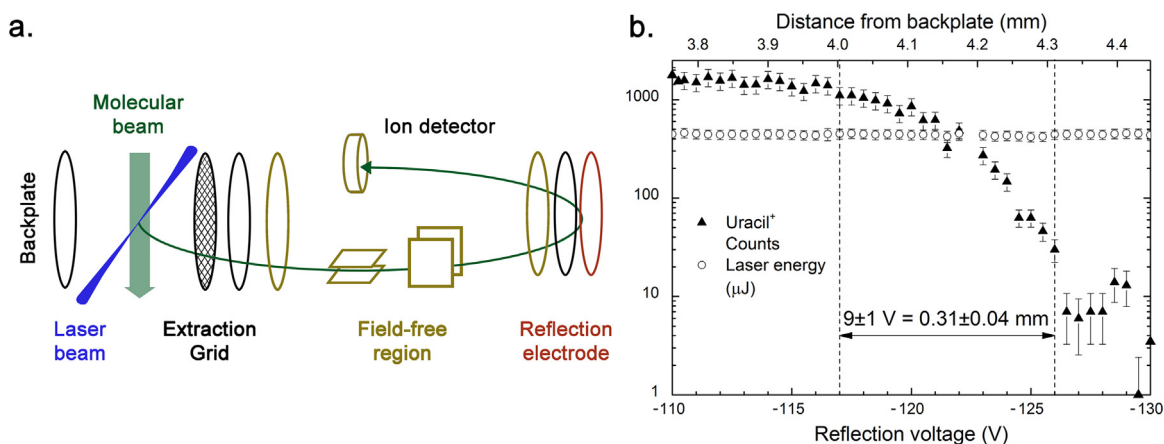
system was based on a *LabView* application interfacing with the TDC card and a laser pulse energy meter (*Spectrum Detector SPJ-D-8*).

The average laser pulse energy was adjusted using the delay between the pulses triggering the xenon flash lamps and the *Q-switch* of the Nd:YAG laser. A convex lens on a slider was used to modify the laser spot diameter at the interaction with the molecular beam and hence control the fluence. This was previously estimated using simple ray diagrams for partially defocused measurements [11,22] but we did not have a reliable method to determine the spot diameter close to the focal point. This problem was solved by recording MPI signals as a function of the voltage on the reflection electrode (see Fig. 1). For non-dissociative ionization (zero kinetic energy release), the key condition for detection was that the voltage at the point in space where the ion was produced should be closer to ground than the voltage on the reflection electrode (the *reflection voltage*). If not, the ion would hit the electrode and would not be reflected towards the detector. Hence, the reflection voltage did not affect the ion signal significantly in Fig. 1b until it corresponded to the crossing position of the focused laser spot and the molecular beam. In order to convert the reflection voltage range across which the ion signal fell from its maximum to zero into a measure of the laser spot diameter, the electric field between the grounded backplate and the extraction grid ( $-380\text{ V}$ , 13.0 mm from the backplate) was simulated using CPO-3D software.

## 3. Results and discussion

### 3.1. MPI comparisons of gas-phase uracil, deuterated uracil, and thymine

Fig. 2 compares high-mass ion production from gas-phase uracil (U), deuterated uracil, and thymine (T). The conditions of the target beam (helium seeded with molecules sublimated at 250 °C) and the focused laser beam parameters were the same in all three measurements. No cluster ion peaks were observed. The absence of any signals attributable to protonated nucleobases provides further evidence of negligible clustering in the neutral beams since such species have previously been identified as major dissociation products of nucleobase cluster ions. For example, protonated uracil was detected strongly in an MPI study of hydrated uracil clusters [11] and electronic structure calculations have shown that the hydrogen-bonded uracil dimer cation relaxes to a proton-transferred form [23]. Similarly, thermochemical calculations have shown that proton transfer from  $\text{T}^+$  to T in a dimer cation is



**Fig. 1.** (a) Schematic diagram of the reflectron mass spectrometer and (b) MPI measurements (220 nm, He 0.8 bar, powder 264 °C) of uracil<sup>+</sup> production as a function of the reflection voltage. The signal cut-off width ( $9 \pm 1\text{ V}$ ) can be directly correlated to the diameter ( $0.31 \pm 0.04\text{ mm}$ ) of the focused laser spot at the intersection with the molecular beam.

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