Photostability of isolated nucleotides under ultraviolet radiation

Abheek Roy[1†] **and S Sunil Kumar**[1]

[1]Indian Institute of Science Education and Research (IISER) Tirupati, 517619, India

The stability of biological molecules under ultraviolet (UV) irradiation has been one of the most extensively investigated problems in molecular photochemistry over the past several decades [1–3]. Among these biomolecules, nucleotides are of particular importance as they constitute the fundamental chemical building blocks of nucleic acids, which encode genetic information and participate in virtually every cellular process essential for life [2]. Photoexcited nucleotide anions, including deoxyadenosine monophosphate ($[dAMP–H]^-$) and adenosine monophosphate ($[AMP–H]^-$), predominantly relax via non-radiative pathways leading to fragmentation. In these systems, photon absorption is followed by internal conversion to the ground state, after which the redistribution of internal energy across vibrational modes leads to statistical fragmentation [4].

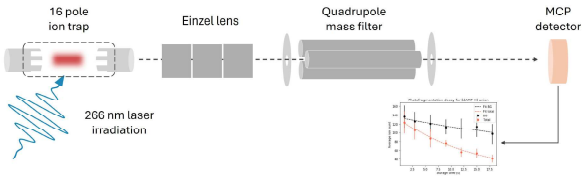

Figure 2: Schematic of the experimental setup for measuring absolute photofragmentation cross sections of trapped nucleotide anions using 266 nm laser irradiation.

In this work, we investigate the UV photofragmentation of isolated $[dAMP–H]^-$ and $[AMP–H]^-$ anions at 266 nm. Absolute photofragmentation cross sections are experimentally determined for both nucleotide systems, providing a quantitative measure of their susceptibility to UV-induced dissociation. Interestingly, despite the structural difference between the deoxyribose and ribose moieties, the measured absolute fragmentation cross sections of $[dAMP–H]^-$ and $[AMP–H]^-$ are found to be comparable within experimental uncertainty, suggesting similar overall photostability under 266 nm irradiation.

To elucidate the molecular origin of the observed fragmentation, time-dependent density functional theory (TD-DFT) calculations are employed to characterize the electronic excitation spectra and relevant excited-state transitions of both anions. Potential fragmentation pathways are subsequently investigated through electronic-structure calculations, with transition-state structures and corresponding barrier heights determined for the different dissociation channels. The calculated barriers are combined with statistical unimolecular rate theory using RRKM analysis. For $[dAMP–H]^-$, an inverse RRKM approach is employed to estimate the effective dissociation barrier by constraining the calculated rates using fragmentation timescales reported in the literature. For $[AMP–H]^-$, the calculated transition-state barrier is used within the RRKM framework to estimate the unimolecular fragmentation rate at the 266 nm excitation energy.

The combined experimental and theoretical analysis links photofragmentation cross sections with molecular structure, dissociation barriers, and fragmentation dynamics, providing insight into the UV response of $[dAMP–H]^-$ and $[AMP–H]^-$ anions

References

[1] Hussain R. *et al.* 2018 *Molecules* **23** 1906
[2] Rastogi R. P. *et al.* 2010 *J. Nucleic Acids* **2010** 592980
[3] Serrano-Andrés L. *et al.* 2008 *Chall. Adv. Comput. Chem. Phys.* **5** 435–472
[4] Sunil Kumar S. *et al.* 2011 *J. Phys. Chem. A* **115** 3483–3490

†E-mail: abheek.roy@students.iisertirupati.ac.in