

Investigating the effect of charge on the intrinsic electronic spectrum of ATP and ADP.

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Over recent years, a growing number of gas-phase studies have been performed on isolated nucleobases and nucleotides to investigate the detailed mechanisms by which these molecules dissipate energy following photoexcitation. There is particular interest in the way that excess electric charges (protonation or deprotonation) can affect such processes.

In this study, we focus on adenosine triphosphate (ATP) and adenosine diphosphate (ADP) mono and doubly charged anions, by investigating the excited states decay dynamics, complementing a previous study on fragmentation processes of the ground state (1). ATP is the cellular principal energy reserve (2). At physiological pH, in the cellular environment, it has four negative charges (1), while in the gas phase the most abundant species, observed via ESI, is doubly charged.

Our technique combines electrospray (ESI) mass spectrometry with UV laser spectroscopy. It allows to isolate ions in the ion trap and study their UV absorption in the gas phase (photodepletion), investigating the electronic decay pathways. The use of the ion trap detector permits, in fact, the study of the produced photofragments thus, giving a picture of the photochemistry and photophysics of the ions (3).

The two ATP anions ($[\text{ATP-2H}]^{2-}$ and $[\text{ATP-H}]^{-}$) show similar photodepletion spectra (Figure). In both cases the photoproducts show fragmentation on the phosphate chain and intact nucleoside. Moreover, photoexcitation of the $[\text{ATP-2H}]^{2-}$ dianion allows the investigation of electron detachment processes, via detection of $[\text{ATP-H}]^{-}$.

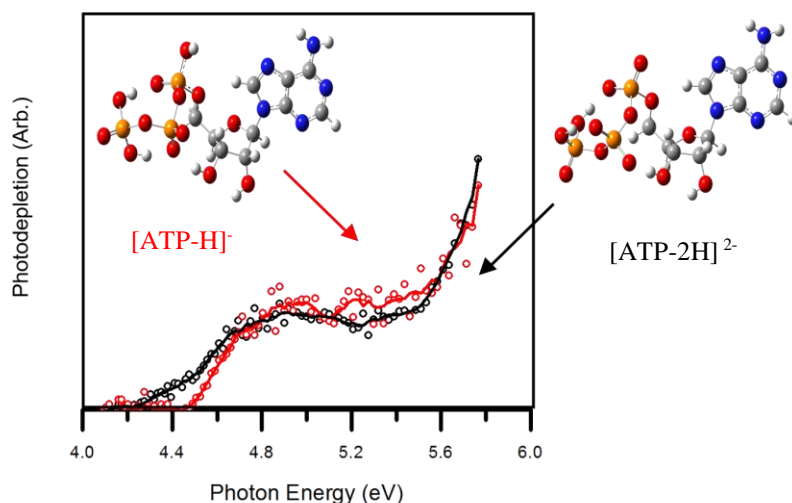


Figure: Structures and photodepletion spectra of $[\text{ATP-2H}]^{2-}$ (black dots) and $[\text{ATP-H}]^{-}$ (red dots). The solid lines are five point adjacent averages of the data points.

References

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