

UV Absorption of Gaseous Nicotinamide, Evidence of Multiple Protonation Sites

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Nicotinamide (NA) is a constituent of the biomolecule NAD, a redox-active coenzyme that is critical in both the metabolism of cell nutrients in the Krebs cycle and the production of ATP in the electron transport chain. NAD is a chromophore in the UV region that changes with the oxidation state of the NA substituent, reduced NAD (NADH) has been shown to photosensitize molecular oxygen to $^1\text{O}_2$ upon UV-A irradiation.(1) It is therefore important to understand the photochemistry and photostability of NA, as this could improve the knowledge surrounding cellular damage caused by sunlight.

Photoaction spectroscopy was used to study the gas-phase absorption of protonated NA; this technique combines mass spectrometry and laser spectroscopy to directly record the absorption spectra of ions,(2) the structures of photofragments can also be determined from the mass spectra. The experimental absorption spectrum (Figure 1) shows influences from several chromophores across the spectral range. Calculated time-dependent density functional theory (TDDFT) excitation spectra, of multiple isomers of protonated NA, corroborate with the experimental absorption spectrum, suggesting that protonated NA can exist in more than one isomeric form in the gas phase.

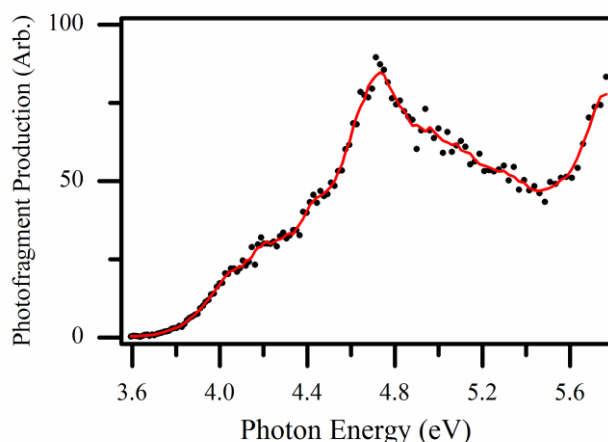


Figure 1: Absorption spectrum of protonated nicotinamide, taken as the sum of the fragments produced by irradiation.

References

- (1) Tanaka, M.; Ohkubo, K.; Fukuzumi, S., *J. Phys. Chem. A*. **2006**, 110, 11214-11218.
- (2) Sen, A.; Dessent, C. E. H., *J. Chem. Phys.* **2014**, 141, 241101.