UV Photolysis Study of *Para*-Aminobenzoic Acid Using Parahydrogen Matrix Isolated Spectroscopy

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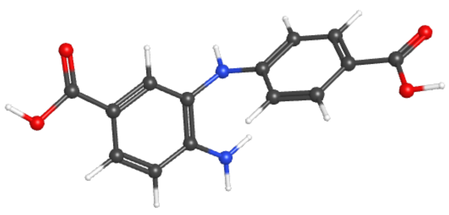
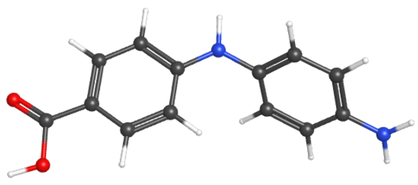
Abstract *Para*-aminobenzoic acid (PABA) is one of the original sunscreen chemical agents. As these agents often undergo photodissociation during the process of UV absorption, understanding the photochemical behaviour of sunscreen agents is highly important. In this study, the photolysis of PABA was studied at three different UV ranges (UVA: 355 nm, UVB: >280 nm, and UVC: 266 nm and 213 nm) using parahydrogen (pH$_2$) matrix isolation Fourier-Transform infrared (FTIR) spectroscopy. PABA was found to be stable under UVA irradiation. However, PABA dissociated into 4-aminylbenzoic acid (the PABA radical) through amino hydrogen atom loss under UVB and UVC irradiation.[1] The production of the PABA radical supports a previously proposed mechanism of the formation of the carcinogenic PABA-thymine adduct. The infrared spectrum of the PABA radical was analyzed with quantum chemical calculations. Two conformers of this radical were observed in the pH$_2$ matrix. Both conformers of the PABA radical were stable in solid pH$_2$ for hours after irradiation. This work displays that pH$_2$ matrix isolation spectroscopy is effective for sunscreen agent photochemical studies.

Introduction

- PABA is the first active ingredients used in sunscreen (1943)
- Carcinogenic, therefore controversial
- PABA photolysis previously studied in solution
- Photoproducts formed via self-reactions[2]



4-(2'-amino-5'-carboxyl)aminobenzoic acid

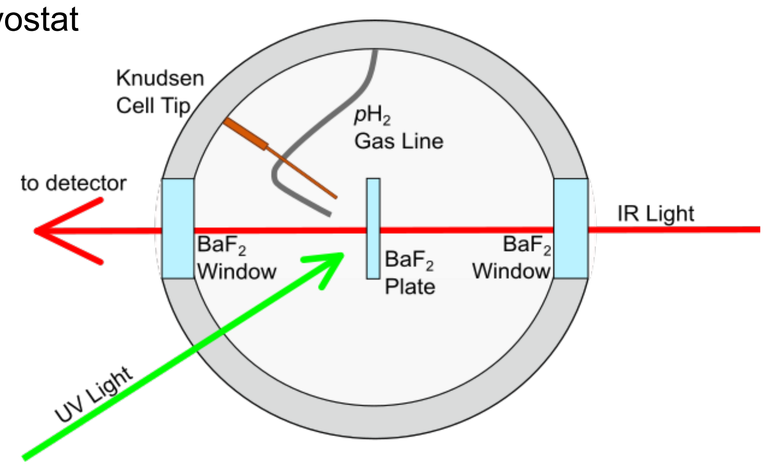


4-(4'-aminophenyl)aminobenzoic acid

- Matrix isolation can isolate unstable molecules
- pH$_2$ matrices: weak cage effects allow radicals to escape lattice site[3]
- pH$_2$ matrices have narrower peaks, producing more detailed spectra[3]
- pH$_2$ is a rotational spin state of H$_2$ (antiparallel nuclear spin)
- At room temperature, H$_2$ is ~ 75% oH$_2$ and ~25% pH$_2$

Experimental

- Pure pH$_2$ was made at 14.1 K with a magnetic converter
- The pH$_2$ and PABA were deposited onto a BaF$_2$ plate at 3.8 K in a cryostat

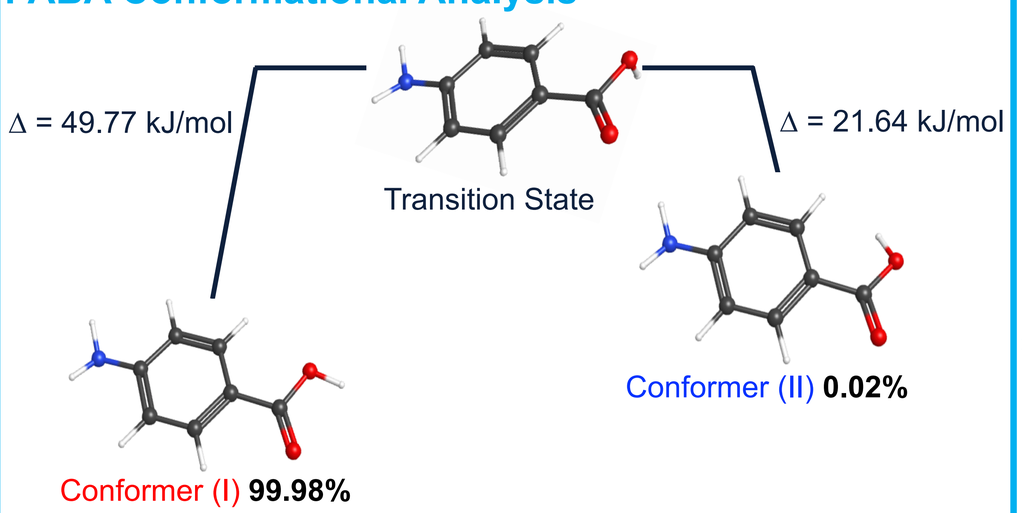


For irradiation:

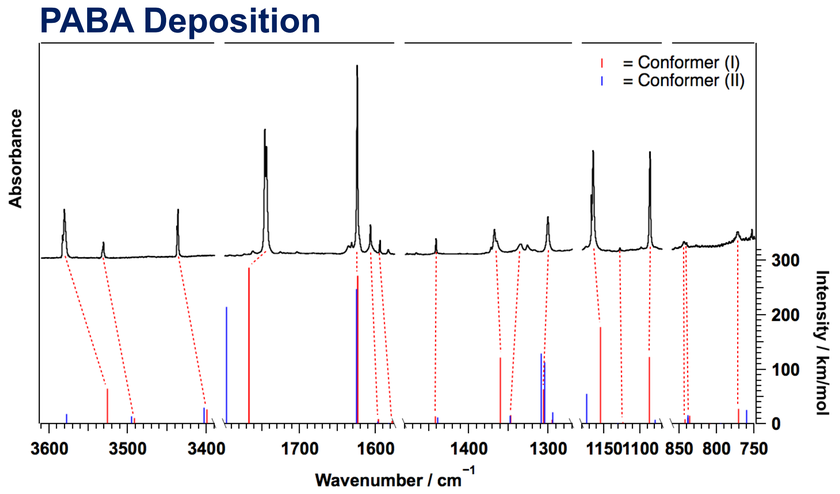
- UVA: 355 nm
- UVB: > 280 nm
- UVC: 266 nm and 213 nm

Theoretical calculations used Gaussian 09 and B3LYP/cc-pVDZ anharmonic

PABA Conformational Analysis



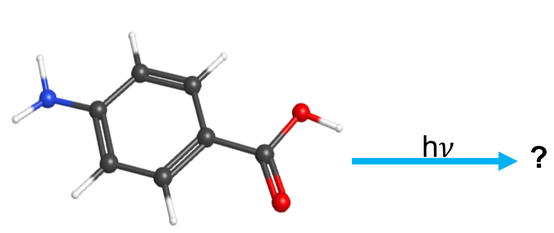
PABA Deposition



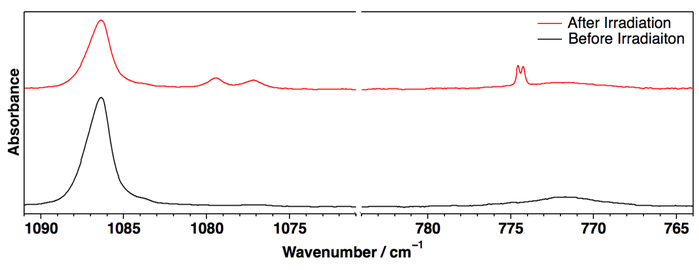
Only Conformer (I) was observed

PABA Photolysis

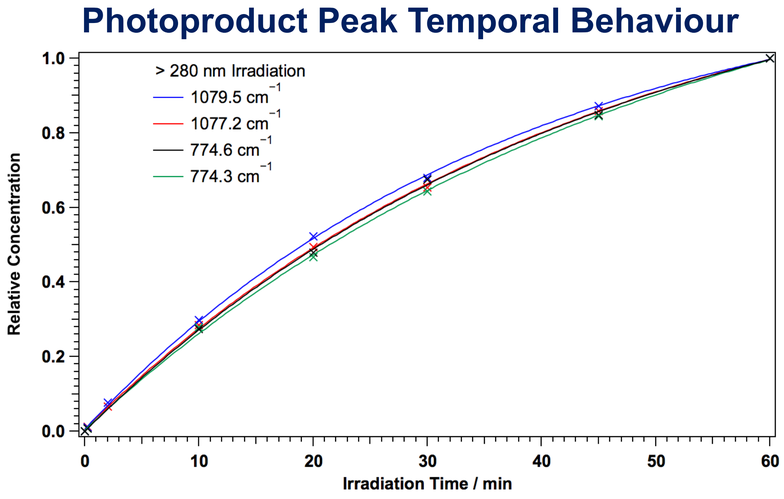
- PABA photolysis not observed following 355 nm irradiation
- Similar photolysis observed following >280, 266, and 213 nm irradiation



Raw Data Before and After Irradiation

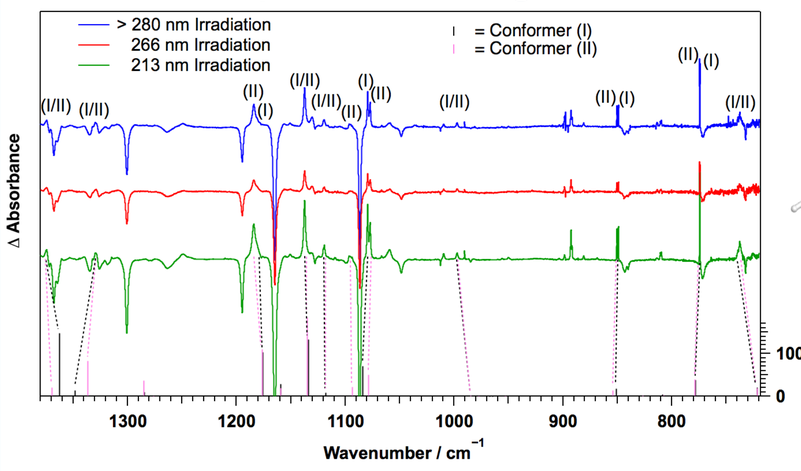


Photoproduct Peak Temporal Behaviour

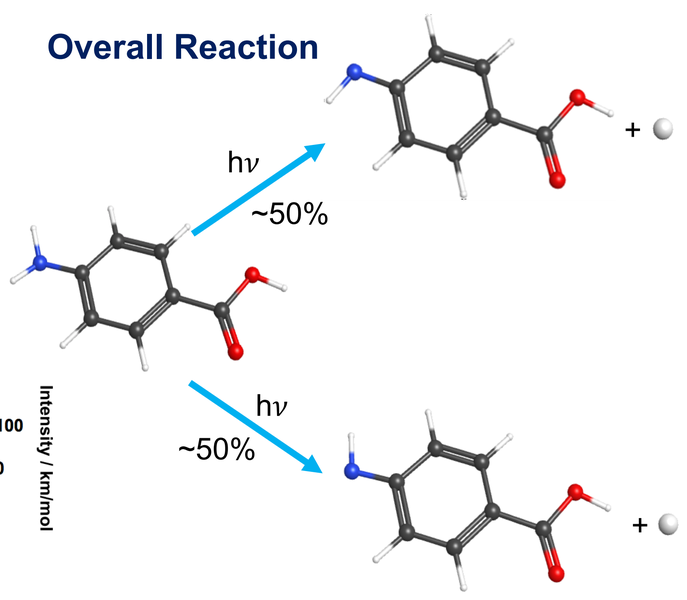


- Photoproduct peaks showed correlation to each other and anticorrelation to PABA decay
- Peaks were close to PABA peaks, suggesting similar structure
- Neither direct decarboxylation nor direct deamination were observed
- Peaks assigned to PABA radical

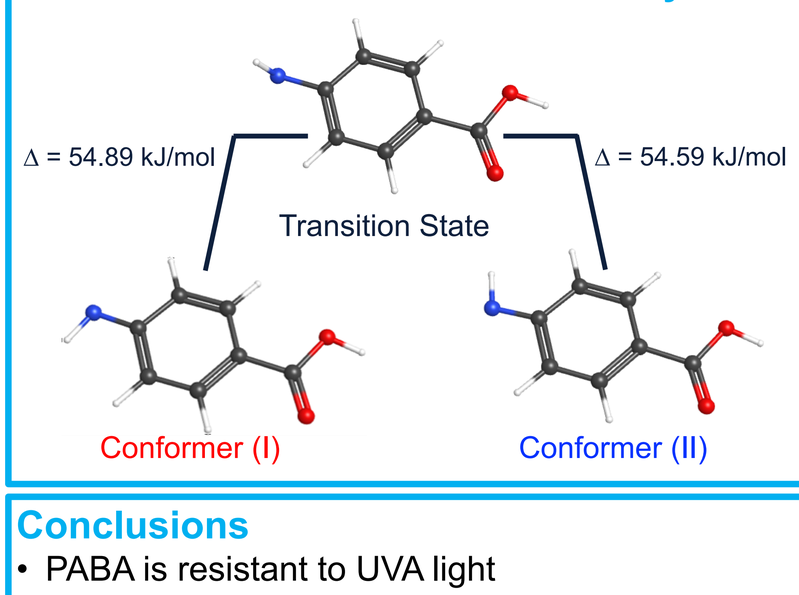
Difference Spectra Following Irradiation



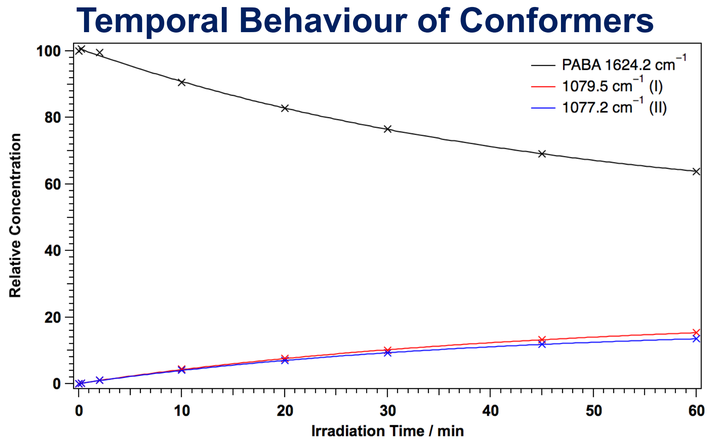
Overall Reaction



PABA Radical Conformational Analysis



Temporal Behaviour of Conformers



Conclusions

- PABA is resistant to UVA light
- PABA loses an amino hydrogen atom following UVB and UVC irradiation, forming the PABA radical
- This work supports photoproducts observed from PABA photolysis in solution and in the presence of thymine, forming the carcinogenic PABA-thymine adduct[4]

Acknowledgements

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References

1. McKinnon, A. et. al. *Photochem.* **2022,** *2,* 88-101.
2. Shaw, A.A. et. al. *Photochem. Photobiol.* **1992**, *55*, 657–663.
3. Momose, T.; Shida, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1 – 15.
4. Shaw, A. A. et. al. *Photochem. Photobiol.* **1992,** *55,* 647 – 656.