



Canadian Association  
of Physicists

Association canadienne  
des physiciens et physiciennes

Contribution ID: 4309 Type: Oral Competition (Graduate Student) / Compétition orale (Étudiant(e) du 2e ou 3e cycle)

## (G\*) Significant Effects of Protonation on the Nature and Kinetics of Isomerization in Molecular Azo Photoswitches

Tuesday 28 May 2024 17:15 (15 minutes)

Molecular azobenzene photoswitches have long been attractive in the design of photoresponsive materials owing to their reversible light-triggered photoisomerization about the azo bond (N=N) between *trans* and *cis* isomeric configurations. Towards more versatile materials applications, azopyridines have been designed as a next-generation azobenzene photoswitch possessing pH sensitivity, hydrogen-bonding, and metal binding abilities. As a result, they have become a key element in the photocontrol of liquid crystals, pharmacological agents, photodriven oscillators, and molecular spin switches. Our group is also developing a new, nature-inspired optical oxygen sensor for tumours whose quantitative readout is the isomerization rate of an azopyridine photoswitch unit. However, detailed studies on the isomerization kinetics of azopyridines and their protonated forms are still lacking. Not only would such studies extend their application to biological contexts, but protonation can also serve as a tool to significantly modulate the photoisomerization process and has even been shown to abolish it entirely. Moreover, there is a conspicuous lack of literature on the photoisomerization of azopyridines in chlorinated solvents where adventitious protonation can occur.

In this work, irradiation of 4-phenylazopyridine (AzPy) in chlorinated solvent with 365 nm light produced significant bathochromic shifts in the  $\pi$ - $\pi$  and  $n$ - $\pi$  absorption bands rather than the expected spectral changes associated with *trans-cis* photoisomerization. In addition, there was a significant acceleration of the *cis-trans* back-isomerization rate, which was attributed to protonation of AzPy at the pyridine nitrogen due to HCl production from UV-mediated photodecomposition of the solvent. Calculations with the density functional theory quantum-mechanical method demonstrated that due to weakening of the electronics of the azo bond, protonation reduced the activation barrier for *cis-trans* isomerization significantly, corresponding to a 9-fold acceleration in the isomerization rate. Remarkably, protonation also shut down intersystem crossing between singlet and triplet potential energy surfaces along the isomerization reaction coordinate.

### Keyword-1

Photoswitches

### Keyword-2

Protonation

### Keyword-3

Photoisomerization

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**Session Classification:** (DPMB) T3-3 Biomolecular Condensates | Condensats biomoléculaires (DPMB)

**Track Classification:** Technical Sessions / Sessions techniques: Physics in Medicine and Biology / Physique en médecine et en biologie (DPMB-DPMB)