

Proton Transfer and Hydrogen Transfer in Photorelaxation of Indigo

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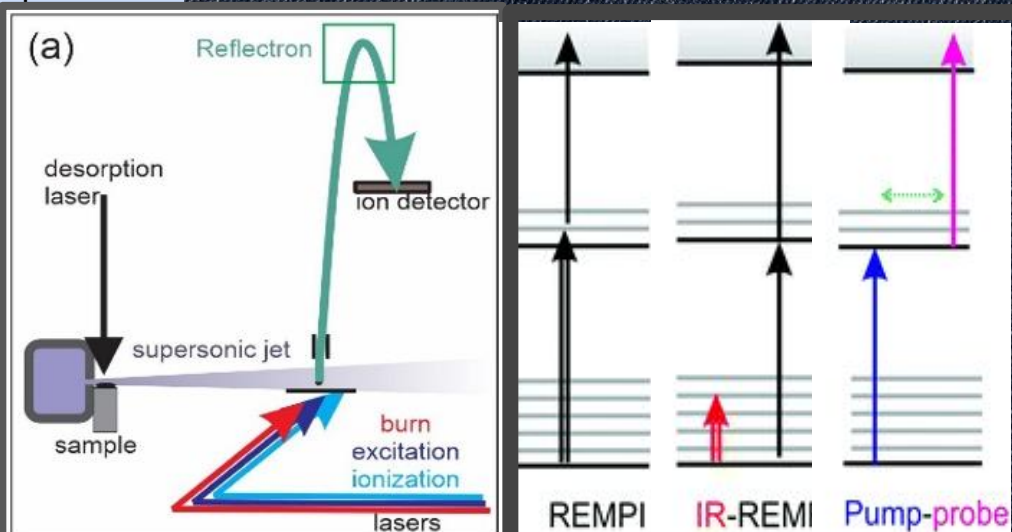
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Indigo is the dye that makes jeans blue. It was already used in ancient cultures, and some of their artifacts retain their distinct blue color to this day. Indigo thanks this tremendous photostability to ultrafast return to the ground state from the excited state. The photophysics of indigo can be very sensitive to its environment, and to understand the fundamental properties of the chromophore, we studied the intrinsic photodynamics of isolated indigo in the gas phase. We observed a barrier to relaxation of about 700 cm⁻¹, beyond which decay was dominated by fast excited state dynamics. Below this barrier we observed slow decay and, computation at the ADC(2)/MP2/cc-pVDZ level predicts two competing processes that each lead to tautomerization from the di-keto to the keto-enol form with intramolecular proton transfer, occurring in the order of 1 nanosecond and intramolecular hydrogen transfer, occurring in the order of 10 nanosecond. Both cases undergo drastic charge distribution changes upon de-excitation.

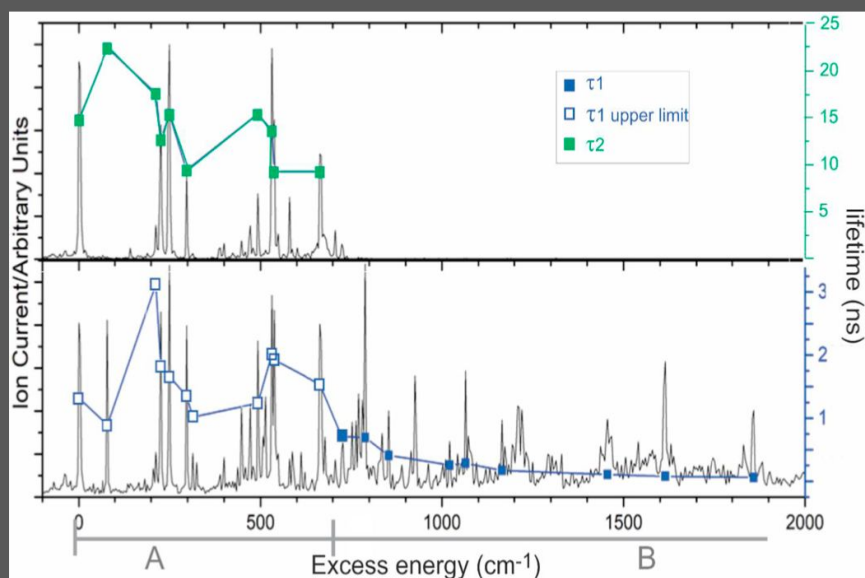
Experimental



Indigo was laser desorbed at 1064 nm, jet cooled in argon, resonantly 2-photon ionized using (R2PI) with the ions detected in a TOF mass spectrometer.

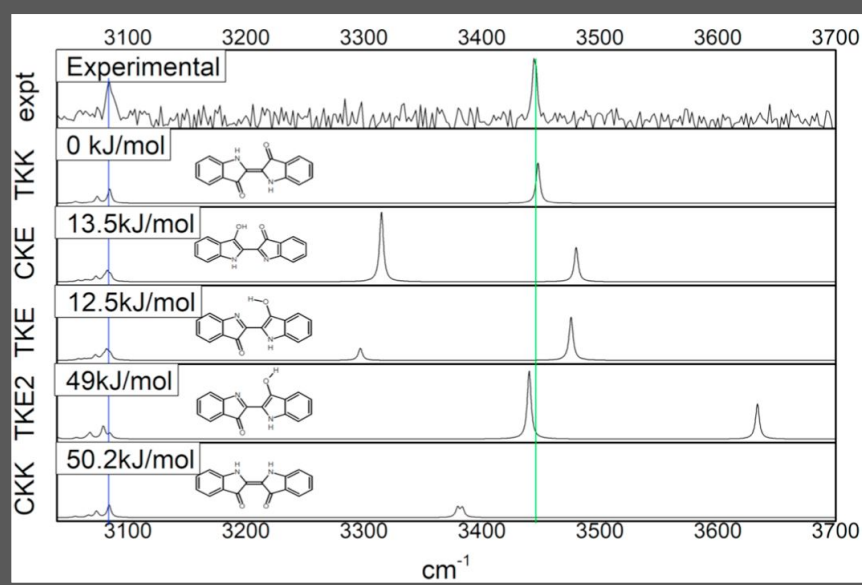
Pump-Probe experiments were performed in both the picosecond and nanosecond regimes with a 30 ps 213 nm or a ns 193 nm probe, respectively

R2PI spectra and ES lifetimes



2C-R2PI spectra collected using ps excitation followed by ionization with ns pulses on top, and ps pulses on bottom. Squares are the lifetimes as recorded from pump-probe experiments in the ns (green) and ps (blue) range. Below 700 cm⁻¹, in spectral range A, the lifetimes show the presence of multiple components. Above 700 cm⁻¹, in spectral range B, only a single timescale component was observed.

IR-UV hole burning & vibrations

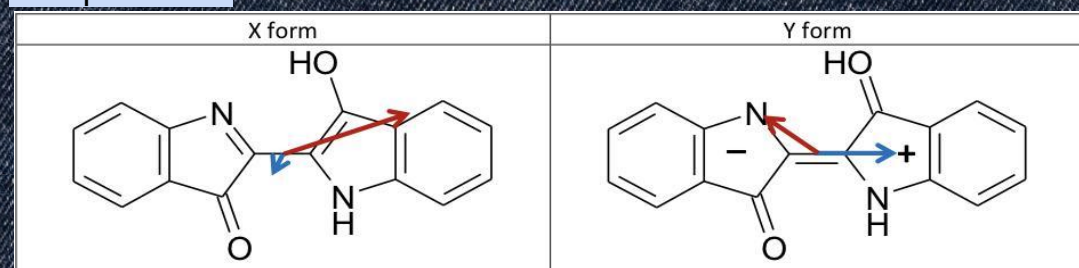


IR-VIS double resonance spectroscopy data (Top) of indigo, taken at origin, 18,129 cm⁻¹ with vibrational frequencies of the lowest energy tautomers. The experiment matches the calculated trans-diketo tautomer.

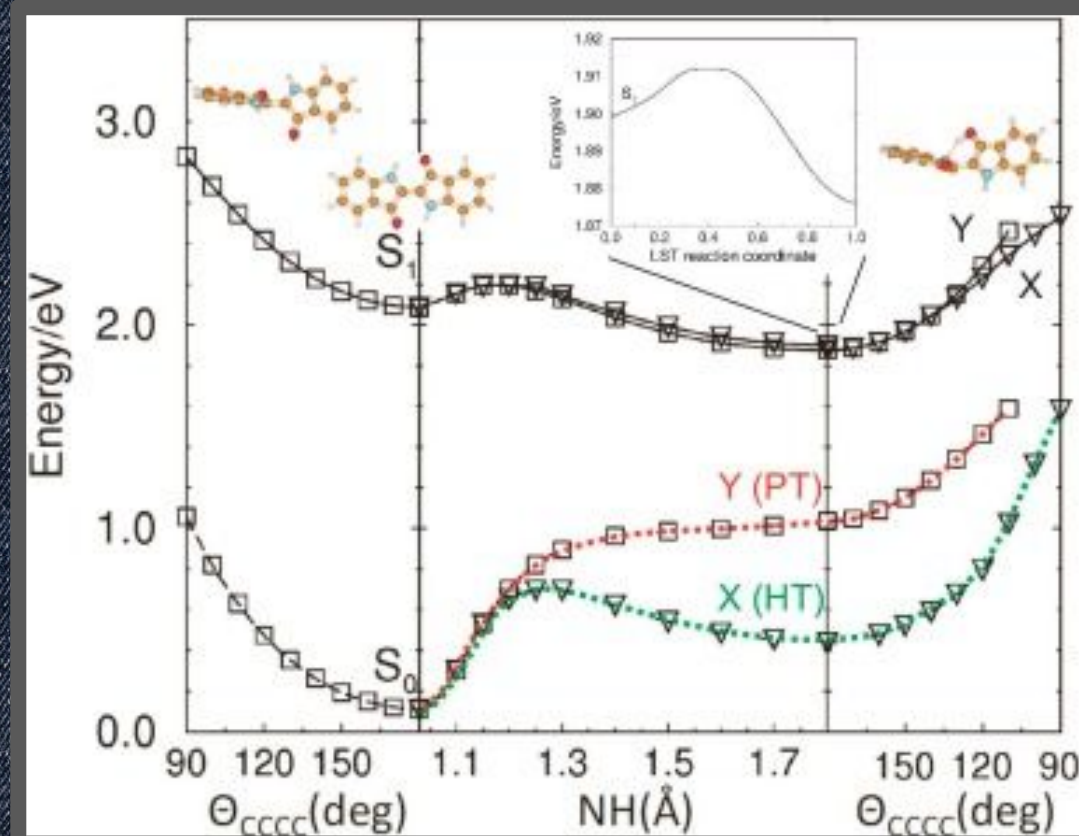
Summary & Future Plan

Unlike the common ESIP, Indigo also exhibits hydrogen transfer as part of its photorelaxation. Two deactivation processes were observed experimentally. Computational modeling features alternating proton transfer and hydrogen transfer, in the excited state and in the ground state. Partitioning between the two pathways depends strongly on vibrational modes. Above 700 cm⁻¹, the excited state lifetime shortens significantly, providing a safe relaxation mechanism that leads to indigo's stability against radiative damage. **Follow-up studies with single and double deuterated indigo are underway to further elucidate the excited state dynamics.**

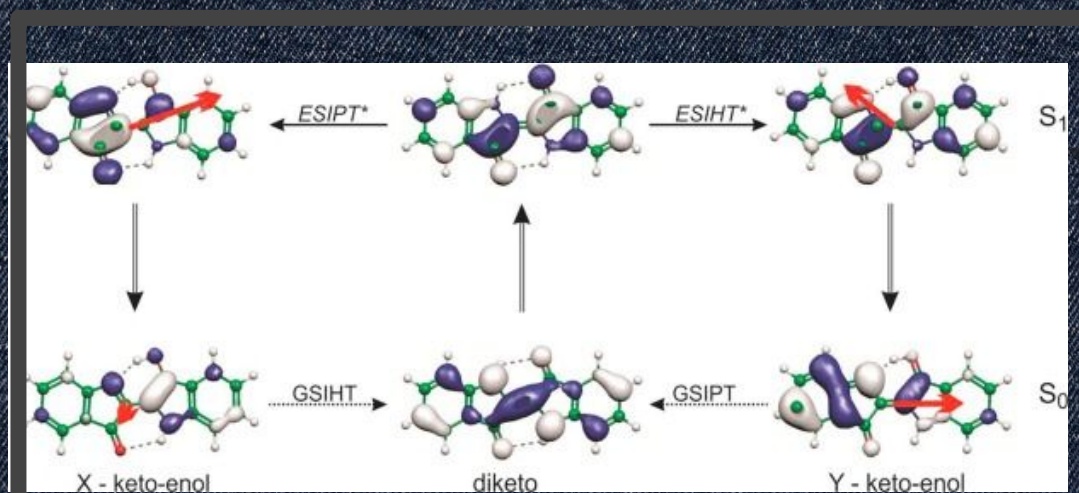
Computational



Geometric structures of the X and Y enol-keto forms of indigo. Arrows illustrate direction and relative value of dipole moments computed for the S₀ state (blue) and for the S₁ state (red) at the S₁ optimized geometry.



PE profiles of the S₀ and S₁ states of indigo were computed along the minimum energy paths optimized in the S₁ state for the PT coordinate (NH distance)-central panel, and the inter-ring twist coordinate (CCCC dihedral angle) of the di-keto (left panel) and the keto-enol (right panel) tautomers. Solid lines indicate minimum energy profiles of the S₁ state. Dashed lines indicate vertical energy profiles of the ground state computed at the geometry of the S₁ state. PE profiles of the X and Y forms are represented by squares and triangles respectively. The red color indicates PT and the green color indicates H-atom transfer. A significant reduction of the S₁ - S₀ energy gap for the Y form of the keto-enol tautomer (0.84eV) as compared to the X form (1.47eV) provides the source of more efficient radiation-less decay of electronic excitation of the former



Transitions between the tautomeric forms of indigo in ground and excited states with electron orbitals involved in transitions and dipole moments in red arrows

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