

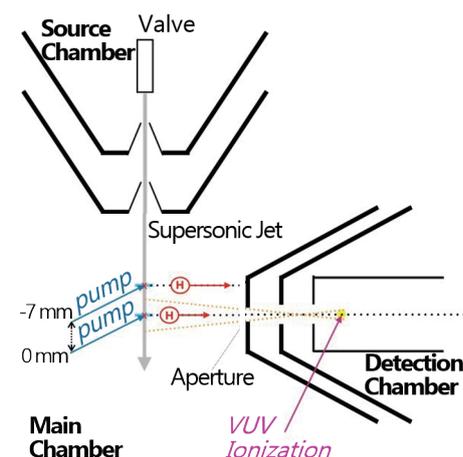
Relaxations of a UV-Excited Bio-Chromophore

An aromatic bio-chromophore under UV irradiation was found to possess a spin-flip path to compete with the well known $\pi\pi^*/\pi\sigma^*$ conical intersection.

After absorbing an ultraviolet (UV) photon, a bio-chromophore initiates complicated mechanisms to relax the photon energy through electronic-nuclear coupled motions. At particular excitation wavelengths, the photon energy could be dissipated into heat to prevent decomposition; in other cases, that energy might trigger an evolution to form new molecules after a sequence of chemical reactions. Such a decisive selection criterion provided by UV light has determined the molecular architecture of life at the beginning of biogenesis. The intrinsic molecular mechanism shown in Fig. 1, internal conversion (IC) of UV-excited aromatic units between electronically excited $\pi\pi^*$, $\pi\sigma^*$ and ground states through conical intersections (CI), is a particularly intriguing problem for understating excited potential-energy surfaces (PES, *i.e.*, resulting from the forces responsible for binding atoms into a molecule) and nonadiabatic dynamics in multi-dimensional nuclear coordinates (*i.e.*, the energy flow *via* electronic-nuclear coupling). Since about year 2000, considerable concern has arisen over the strong effect of the repulsive $\pi\sigma^*$ state along X–H (X: N, O, S) bonds in aromatic molecules. In NSRRC, by applying a novel time-selected photofragment translational spectroscopic (TS-PTS) method to aniline, we report an unexpected dissociation channel mediated by triplet states, which competes with the reaction path *via* $\pi\pi^*/\pi\sigma^*$ CI.

Shih-Huang Lee (NSRRC), Yin-Yu Lee (NSRRC), Chi-Kung Ni (Academia Sinica) and Chien-Ming Tseng (National Chiao Tung University) recently modified the universal crossed-molecular-beam machine using synchrotron vacuum-ultraviolet light as an ionization source to the new TS-PTS method.¹ They investigated the dynamics of photodissociation of phenol, the chromophore in amino-acid tyrosine, determining the distributions of translational energy and the

branching ratios of the phenoxy radicals produced in states X, A and B with no background from undissociated hot molecules.² Here, by TS-PTS, they unambiguously provided the first experimental observation of the distribution of translational energy in triplet-state dissociation of aniline unhindered by a background of multiphoton dissociative ionization affecting conventional methods as shown in Fig. 2.³



TL S 21A1 Schematic of the apparatus for time-selected PTS. [Reproduced from Ref. 3]

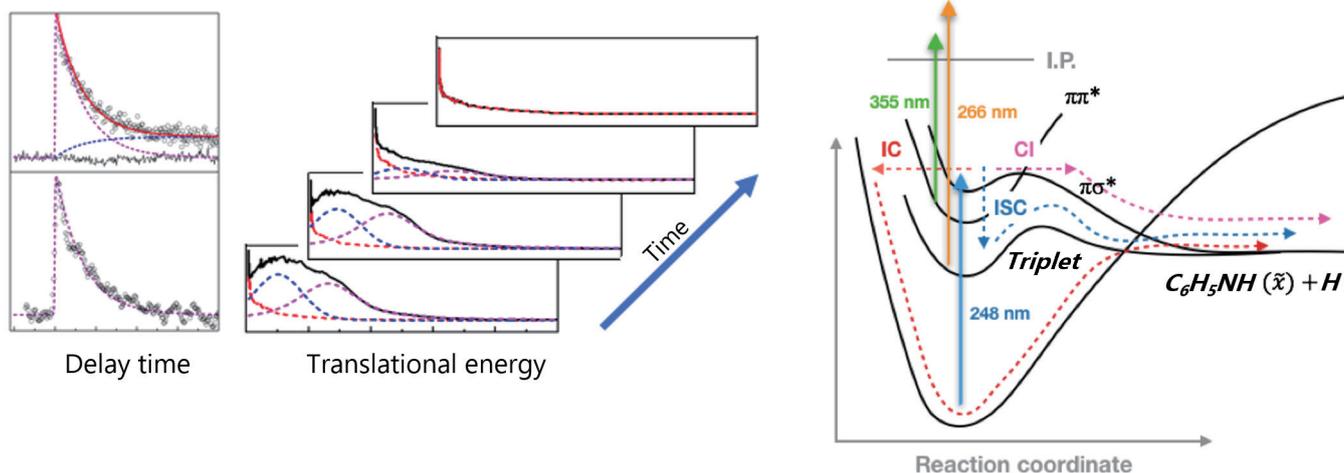


Fig. 1: Schematic figure of ISC, CI, and ISC as well as the corresponding data from crossed-molecular-beam machine. [Reproduced from Ref. 3]

They confirmed intersystem crossing (ISC) by time-resolved photoion yields (TR-PIY)^{3,4} with selective probing of the population changes of S_1 and triplet states as shown in Fig. 3. They uniquely combined TS-PTS and TR-PIY to elucidate the relative ionization cross sections of S_1 and triplet states at 266 nm, thus demonstrating a determination of the branching fractions, excited-state lifetimes and rates of ISC upon excitation at a few wavelengths. These data will be useful for comparisons with theoretical calculations.

The characteristics discovered in this research indicate that the competitive ISC of aniline against relaxation paths *via* CI is a novel aspect of aromatic chromophores containing coupled PES. They provided the first direct experimental evidence of such multifurcation dynamics (ISC vs. CI, and IC in Fig. 1) occurring along with the repulsive $\pi\sigma^*$ state in the aromatic systems. These results open an alternative new understanding of the excited-state dynamics of aniline. This work should hence be of interest to a broad readership, including those studying nonadiabatic dynamics, spin-orbital coupling and photochemistry in the excited states of aromatic molecules. (Reported by Chien-Ming Tseng, National Chiao Tung University)

This report features the work of Chien-Ming Tseng and his collaborators published in J. Chem. Phys. 151, 141101 (2019).

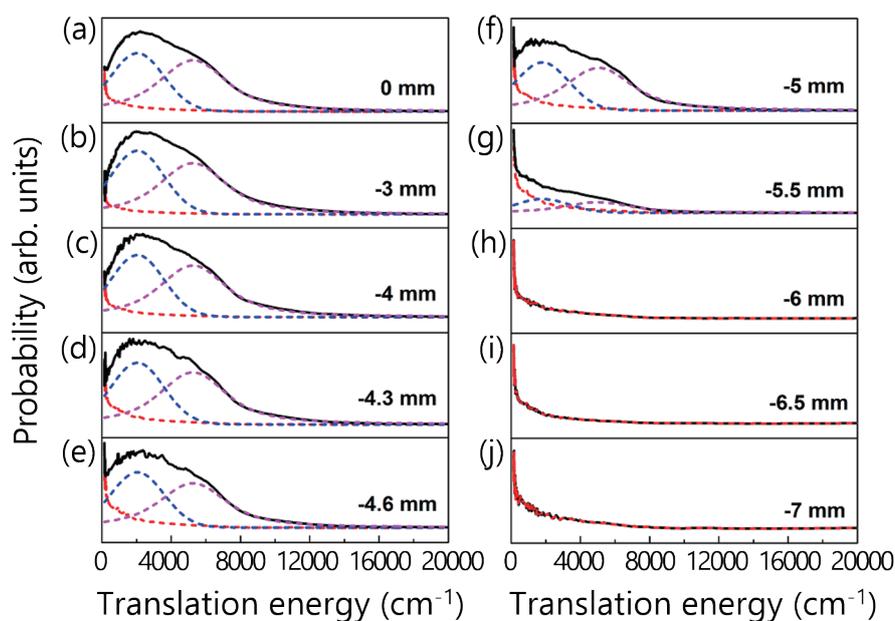


Fig. 2: (a)–(j) Distributions of translational energy for the H-atom elimination channel at 248 nm as a function of the pump laser position. Magenta and blue dashed lines represent two rapid components; a red dashed line represents the slow component. [Reproduced from Ref. 3]

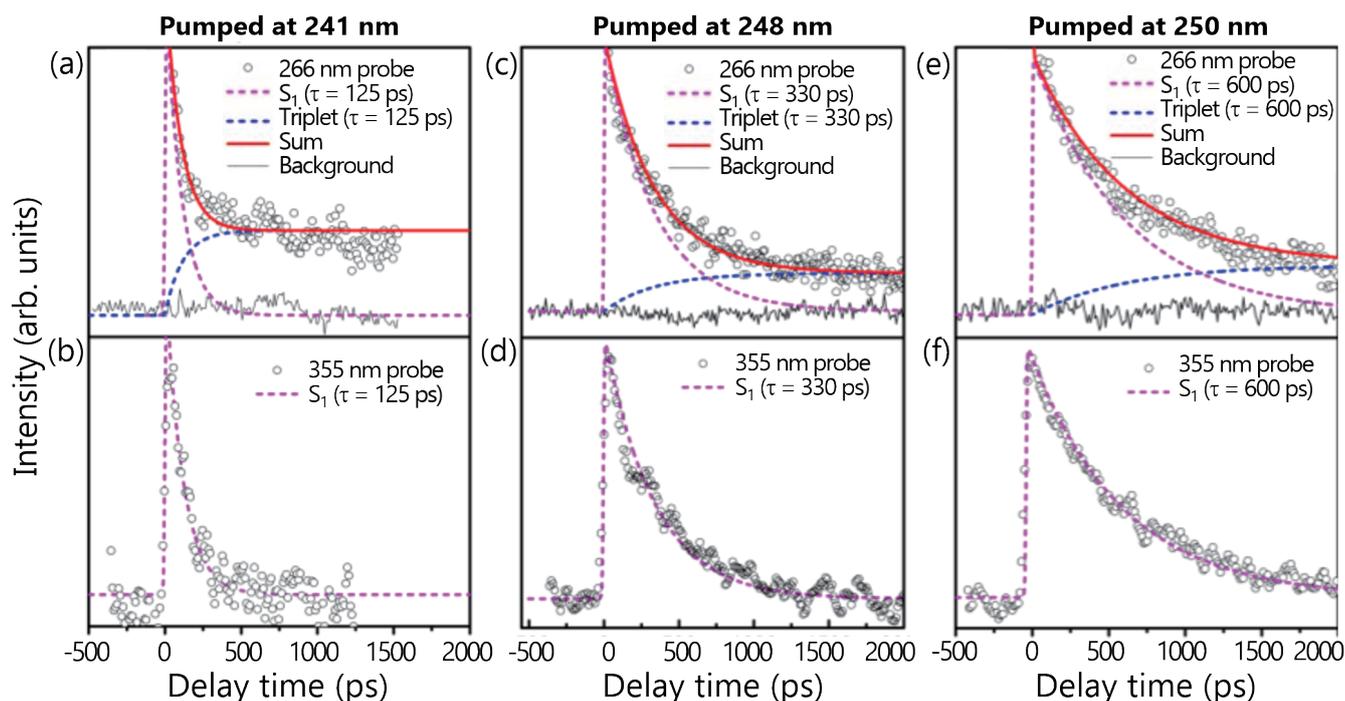


Fig. 3: TR-PIY of aniline upon excitations at (a)–(b) 241 nm, (c)–(d) 248 nm and (e)–(f) 250 nm. The black circles in the upper panel, (a), (c), and (e), and the lower panel, (b), (d), and (f), are experimental measurements of ion yields using a probe laser beam at 266 and 355 nm, respectively. [Reproduced from Ref. 3]

TLS 21A1 U90 – (White Light) Chemical Dynamics

- Photofragment Translational Spectroscopic
- Molecular Science, Chemistry, Gas phase, Photochemistry, Excited-state Reaction Dynamics

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New Insight into the Structure of Biogenic Amorphous Calcium Carbonate

X-ray absorption spectra recorded at ambient water vapor indicates that the structural transformation of hydrated amorphous calcium carbonate (ACC) to crystalline calcite is more involved and contains a heretofore overlooked step of nano-calcite formation.

Among six polymorphs of calcium carbonate (CaCO_3), amorphous calcium carbonate (ACC) is the least stable and transforms rapidly into a crystalline calcium carbonate polymorph such as calcite or aragonite. ACC constitutes a main ingredient in seashell creatures such as urchins, corals, mollusks etc., and is an important precursor phase of biogenic calcite. Researchers have been motivated by this so-called biomineralization in which living organisms, especially micro-organisms, can convert organic substances to inorganic derivatives, to design functional materials for multiple applications.

ACC in at least two distinct forms, *viz.*, types 1 and 2, relevant to the formation of biogenic calcite are postulated based on the study of the growth of sea-urchin larval spicules. ACC of type 1 has been unequivocally assigned to hydrated ACC, whereas the assignment of ACC of type 2 to anhydrous ACC is still under debate. During the spicule growth, the ACC is precipitated from mineral-rich sea water at the growth location and then dehydrates into the transient ACC of type 2 that transforms further into calcite, namely, $\text{ACC}\cdot\text{H}_2\text{O}$ (type 1) – ACC (type 2) – biogenic calcite. This path, although correctly describing the dehydration, provides no indication about the minute structural difference between ACC of these two types.

X-ray absorption spectra (XAS) recorded at the Ca L edge provide useful information about a change of the metal–ligand bonding environment, as experienced by the central Ca atoms during the course of a phase transformation of ACC from hydrated to crystalline form. This technique is hence powerful in addressing the structural transformation. Moreover,

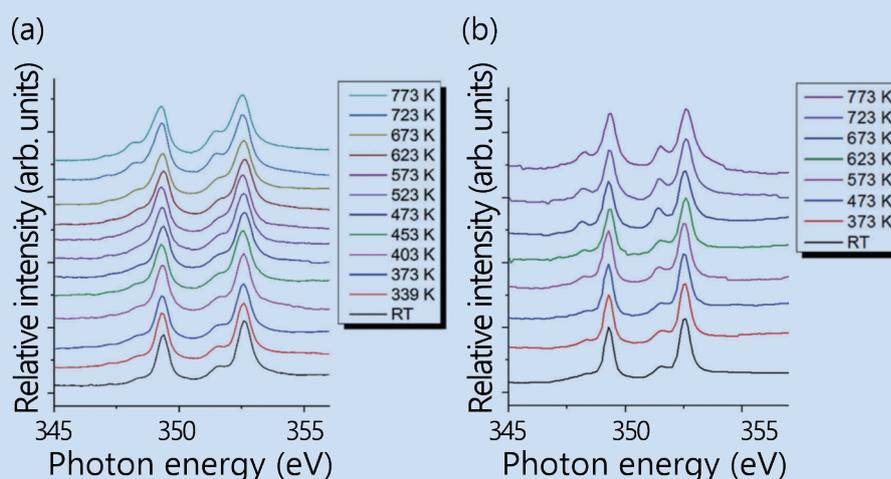


Fig. 1: Ca L edge X-ray absorption spectra of ACC acquired under ultrahigh vacuum (a), and under water vapor at pressure 0.4 mbar equivalent to 1.3% relative humidity (b). Two major features (L_3 and L_2) are separated by a spin-orbit interaction about 3.2 eV; each spin-orbit component is further split by crystal-field splitting (CFS) into two lines about 1.2 eV apart, yielding a smaller shoulder peak at the side of less photon energy. A careful analysis of the CFS parameters based on refined curve fitting provides revealing insight into the structural transformation of ACC. [Reproduced from Ref. 1]