AFRL-OSR-VA-TR-2014-0170

USING VIBRATIONS TO PROBE AND CONTROL PHOTOISOMERIZATION IN LIQUIDS

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07/08/2014
Final Report

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Final Report
FA9550-10-1-0116
Using Vibrations to Probe and Control Photoisomerization in Liquids

The focus of our AFOSR-funded research during this period of support has been studying the influence of vibrational excitation on electronic-excited-state dynamics in a variety of environments. One of the primary focuses is in liquids, and we have studied excited-state dynamics of vibrationally excited stilbene, of a biomimetic switch, an N-alkylated indanylidene pyrroline Schiff base (NAIP), and of a model compound for excited state isomerization, avobenzone. A unique environment in which we have also explored the effects of surroundings on molecular rearrangements is supercritical carbon dioxide, $scCO_2$. Monitoring the excited-state isomerization of salicylidene aniline has shown the role of viscosity on the course of the dynamics.

Vibrationally Excited Stilbene

Figure 1 is a schematic view of the potential energy surfaces for the isomerization from *trans*- to *cis*-stilbene along with arrows indicating the three pulses we use: a vibrational excitation pulse (λ_{vib}), an electronic excitation pulse (λ_{el}), and a broadband visible probe pulse (λ_{probe}). We previously demonstrated that in the halomethanes vibrational energy flows into Franck-Condon active carbon-halogen bonds after excitation of C-H stretching motion. Population of these Franck-Condon active modes shifts the electronic absorption spectrum to lower energy, allowing preferential electronic excitation of vibrationally excited molecules. Because the two-photon experiment requires that we intercept the vibrationally excited molecule while energy is in the Franck-Condon active modes, we measure the vibrational relaxation rates by preparing vibrationally excited *trans*-stilbene and probing the transient ultraviolet absorption of the excited molecules. After initial excitation of the C-H stretching overtone vibration, we observe energy flow into the Franck-Condon active modes within our time-resolution of a few hundred fs and out of these modes in about 400 fs.

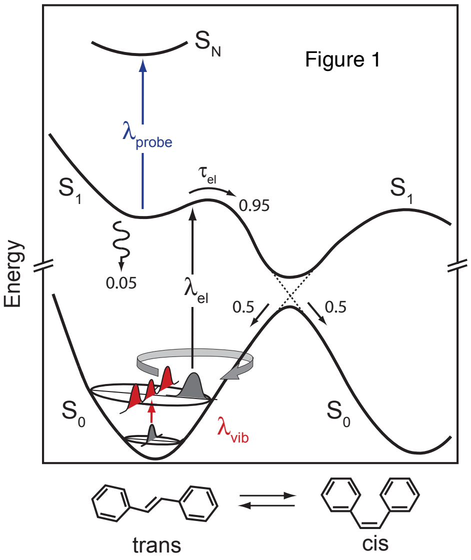
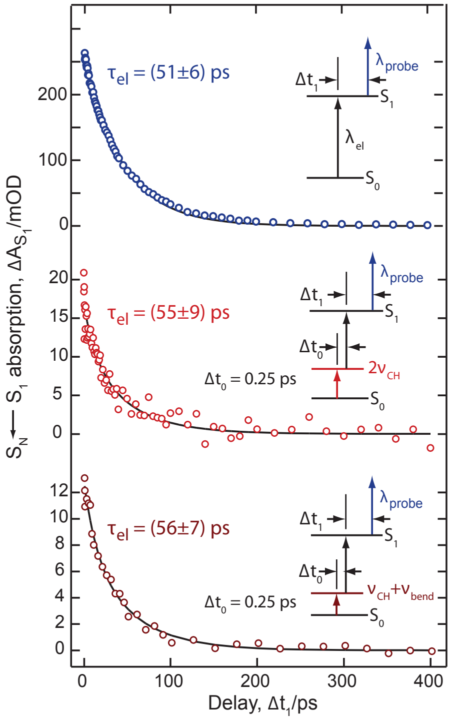


Figure 2



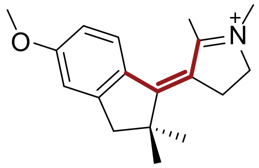
We introduce the electronic excitation pulse (λ_{el}) to promote the vibrationally excited molecules to the S_1 state 250 fs after the vibrational excitation pulse (λ_{vib}) and then monitor the decay of the excited state with the broadband probe pulse (λ_{probe}). Figure 2 shows the 585-nm transient absorption of electronically excited *trans*-stilbene for three different cases: no initial vibrational excitation, C-H stretch overtone excitation, and stretch-bend excitation. In all cases, we select the electronic excitation wavelength to ensure the total energy added is the same. The decay times are all the same within the uncertainty of the measurement and show that the initial vibrational excitation does not alter the excited state dynamics in *trans*-stilbene.

Two aspects of stilbene are likely to be responsible for the insensitivity to the initial vibrational motion. One is the barrier in S_1, illustrated in Figure 1, that controls the passage of the system towards the conical intersection. Because crossing the barrier takes substantially longer than the vibrational relaxation time, it is likely that energy flow randomizes the internal energy and removes any memory of the initial excitation. The other aspect is our preparation of C-H stretching vibrations. We rely on population of Franck-Condon active modes by intramolecular vibrational energy redistribution in the ground electronic state, but we do not choose vibrational modes that have a large component of motion across the barrier and toward the conical intersection. Resonance Raman scattering experiments show that the C=C stretching vibration of the central ethylenic bond has a favorable Franck-Condon character, in keeping with the change in bond order in the excited state. This motion is not necessarily well connected to the torsion and pyramidalization implicated in the *trans*- to *cis*- isomerization.

It may well be that C=C stretching modes are effective in promoting the isomerization in stilbene, but the long barrier crossing time and attendant vibrational relaxation obscure the effect. Thus, the results on the isomerization of vibrationally excited *trans*-stilbene point to criteria for selecting other candidates. We require fast, likely barrierless, electronic dynamics to ensure that the initial vibrational excitation survives long enough to influence the reaction, and, ideally, we should excite directly modes that move the system along the reaction coordinate. These considerations have led us to molecules such as the Schiff base described below.

Excited-State Isomerization of a Biomemetic Switch

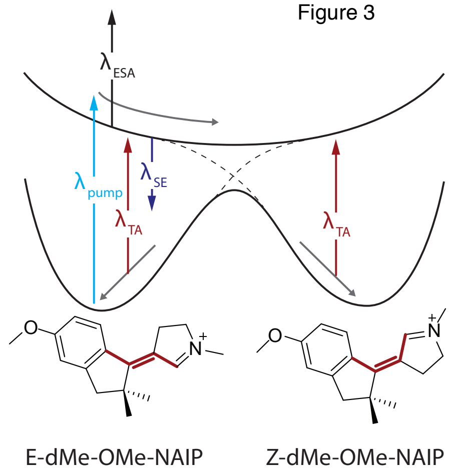
The *N-alkylated indanylidene pyrroline* Schiff bases rapidly isomerize about the central double bond when irradiated with near-ultraviolet light. Our collaborator, Professor Massimo Olivucci of the University of Siena and Bowling Green State University, has combined electronic structure calculations and synthetic expertise to design a series of these compounds that mimic an efficient natural photoswistch, the retinal chromophore in Rhodopsin. The isomerization occurs about the highlighted double bond in the structure of a representative NAIP compound, OMe-NAIP, shown on the right.



The *cis-trans* isomerization of protein-bound retinal is fast and efficient, but these properties disappear when the chromophore is not bound in Rhodopsin. The structure of the NAIP compounds designed by Olivucci and coworkers has three specific goals. The first is to mimic the constraints of the protein environment, a goal they meet with the rigid five-membered rings encapsulating the conjugated p-bond network of NAIP. The phenyl moiety of the indanylidene meets the second goal, extension of the electronic absorption of NAIP into the near ultraviolet region. The third, most practical, goal is to make the synthesis as efficient as possible. The O-methoxy group and quaternary carbon of the indanylidene group facilitate the synthesis.

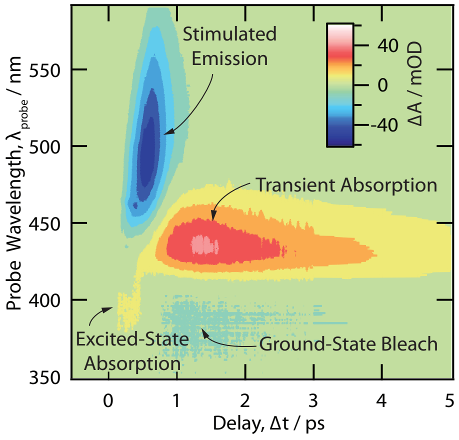
We have collaborated with Olivucci and his group to study the excited-state dynamics of dMe(demethylated)-OMe-NAIP, a relatively simple NAIP compound that has no methyl group proximal to the nitrogen cation, in preparation for experiments on the vibrationally excited compound. These experiments use broadband transient electronic absorption to monitor the evolution of the excited molecule following 400-nm excitation. Figure 3 is a sketch of the potential surfaces on which the isomerization of dMe-OMe-NAIP occurs. The contour plot of Figure 4 summarizes the evolution of the transient electronic absorption that we observe following 400-nm excitation of dMe-OMe-NAIP in methanol solution. As in other NAIP compounds, we see excited-state absorption, stimulated emission, transient absorption, and ground-state bleach features. Analyzing the transient signal at different wavelengths by fitting the evolution to multiple exponentials allows extraction of characteristic times for motion on the excited- and ground-state surfaces. The excited molecule moves to the conical intersection in about 300 fs and takes another 250 fs to reach vibrationally excited levels of the ground state. Complete vibrational relaxation, marked by recovery of the ground-state absorption, requires 5.9 ps.

Figure 3



The timescales suggest the possibility of vibrational mediation and also provide an interesting contrast in their own right. The 300-fs lifetime of dMe-OMe-NAIP is about twice as long as that of other NAIP compounds, and there are essentially no coherent oscillations even though they are prominent the other compounds. A notable difference between the compound we have studied and others is that the equilibrium angle between the five-membered rings is much smaller. Calculations suggest that the greater twisting toward the transition state in the other molecules is enough to enhance the rate of reaction on the upper surface, which should also allow better preservation of coherent motion in those other molecules. The timescale of relaxation for the transient absorption from vibrationally energized photoproducts in NAIP compounds further cements their attractiveness as targets for vibrational mediation, and we are eager to examine the relaxation of dMe-OMe-NAIP after mode-specific infrared excitation.

Figure 4



Excited State Dynamics of Avobenzone

We have also made the first measurements of the femtosecond and picosecond dynamics of avobenzone after excitation at 350 nm. Immediately after excitation, we observe excited-state absorption and stimulated emission from the electronically excited state. Subsequently, the system evolves to for a m vibrationally excited chelated enol and three distinct rotational isomers. The vibrationally energized chelated enols relax *via* primarily intramolecular pathways in 6 ps. One of the isomers avobenzone relaxes in 1.3 ps through hydroxyl group torsion, antoher relaxes in tens of picoseconds through single-bond torsion, and a third persists throughout the timescale of our experiment. We estimate the branching ratio among the three non-chelated isomers by analyzing the amplitude of their corresponding components in the time evolution of the ultraviolet transient absorption.

These dibenzoylmethane compounds, which are widely used as components in sunscreens, have rich photochemistry involving isomerization through multiple pathways after ultraviolet excitation. The photoreactions of dibenzoylmethanes include *cis-trans* isomerization, isomerization about single bonds to form rotamers, and *enol-keto* tautomerization. The variety of photoisomerization pathways present in dibenzoylmethanes makes them an attractive target for fundamental studies of isomerization dynamics.

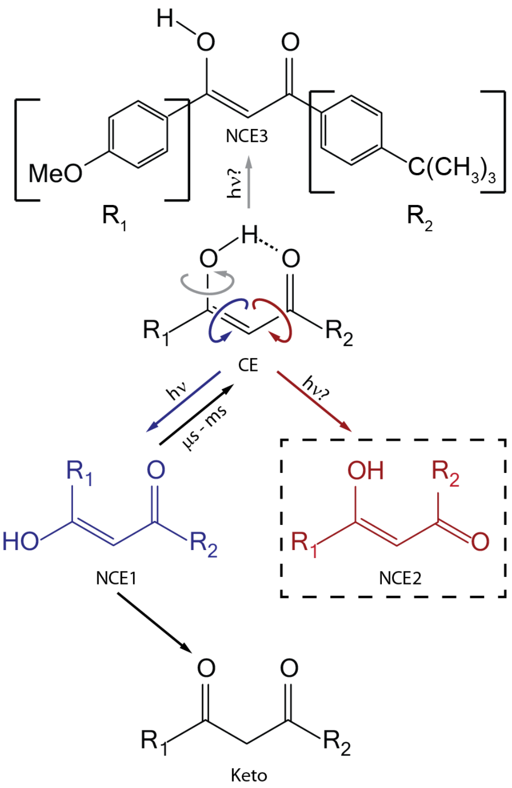
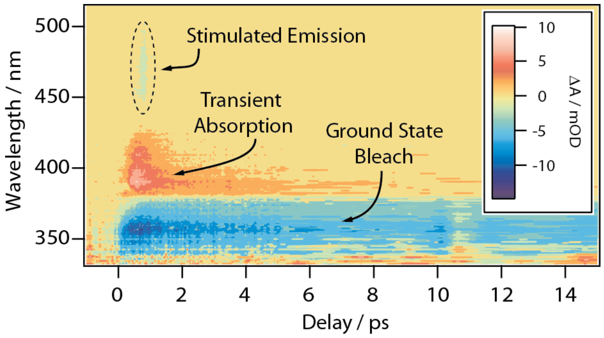


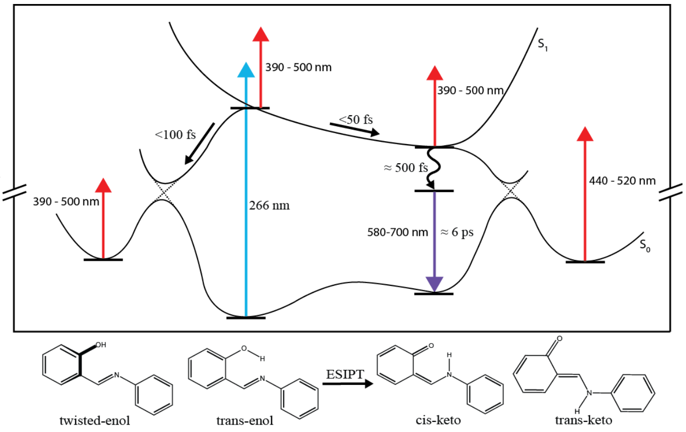
Figure 4 summarizes the excited state chemistry of avobenzone. It exists primarily in a chelated enol (CE) form, characterized by an intramolecular hydrogen bond, in most solvents. Flash photolysis experiments show that a non-chelated enol, designated NCE1, is formed through *cis-trans* isomerization following excitation near the absorption maximum of CE at 350 nm. Analysis of the kinetics of the reverse reaction, the isomerization of NCE1 to CE, suggests an equilibrium between NCE1 and another isomer, NCE2, a rotational isomer formed through rotation about a single bond. Because the barrier to rotation about a single bond is much lower than to *cis-trans* isomerization, leading to much faster relaxation, there is previously no direct observation of NCE2. Rotation about the carbon-oxygen bond of the hydroxyl group after excitation at 350 nm drives the formation of yet another isomer, NCE3. NCE3 likely relaxes to CE even more quickly than does NCE2 since the moment of inertia of this rotation is quite small.

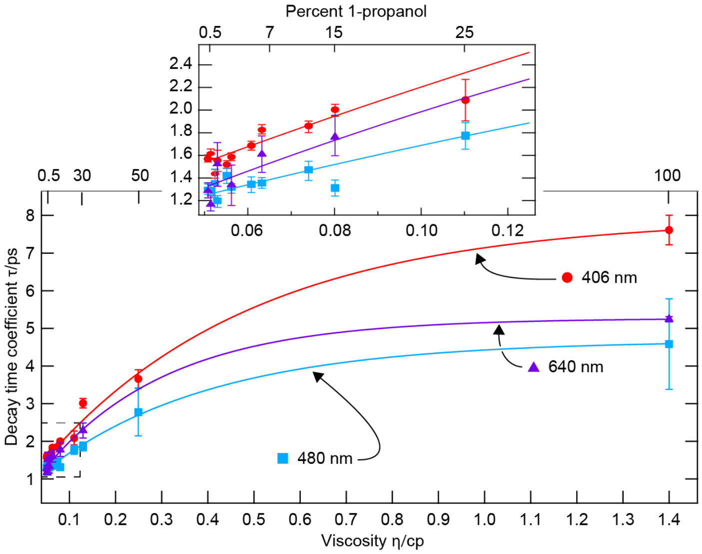
An *enol* to *keto* tautomerization also plays a role in the photochemistry of avobenzone. The *keto* product is a key intermediate in photodegradation of avobenzone. Measurements in different solvents suggest that the *enol* to *keto* reaction is more favorable in the NCE1 geometry than in CE but that protic solvents stabilize NCE1, preventing the reaction to the *keto* isomer. Our work uses ultrafast transient absorption spectroscopy and electronic structure calculations to study the isomerization reactions of avobenzone. We excite avobenzone in the CE form at 350 nm and monitor the differential absorption of the sample at 266 nm, where the non-chelated enol and *keto* isomers absorb more strongly than CE-avobenzone, and between 350 nm and 600 nm, where we observe signatures of electronically and vibrationally excited avobenzone molecules. The signals we obtain with visible probing reveal relaxation from the electronically excited state in hundreds of femtoseconds followed by vibrational relaxation in several picoseconds. Analysis of the dynamics observed with 266 nm light in different solvents, in combination with our calculations, shows that we observe the prompt formation and subsequent decay of NCE2. Long-lived offsets from zero in our transient absorption measurements arise from the comparatively slow dynamics of NCE1 and the *keto* isomer. We find no evidence of reaction from NCE2 to the *keto* isomer, but we do report the first direct measurements of NCE2.



Excited State Dynamics of Salicylidene Aniline in Supercritical CO_2

The influence that different solvent environments have on the reaction dynamics of molecules in solution is a long-standing been a fundamental question with obvious practical consequences. We have used salicylidene aniline, a prototypical excited state intramolecular proton transfer (ESIPT) system, to explore the effect of changing properties of the surrounding environment on the photoisomerization dynamics. We developed an apparatus to preform ultrafast transient absorption experiments in supercritical CO_2, a system in which we can vary the density through temperature and pressure as well as co-solvent fraction, We have used this system to investigate the photoisomerization dynamics of salicylidene aniline in mixed solutions of 1-propanol or cyclohexane and supercritical CO_2, The rate at which the transient absorption signals decay increases as the fraction of co-solvent decreases for both 1-propanol and cyclohexane, The increase in reaction rate scales roughly exponentially with the bulk solvent mixture viscosity, but the dependence is different between 1-propanol and cyclohexane. This behavior suggests that the change in rate arises from contributions of properties besides bulk viscosity, such as solvent polarity or the potential for hydrogen bonding in 1-propanol, The nature of this viscosity relationship to transient absorption decay rates for various characteristic features of the transient absorption spectra and comparisons between 1-propanol and cyclohexane co-solvents provide a window into the reaction mechanism and the influence of solvent on the reaction of SA.





Summary

The AFOSR-supported research has helped paint a picture of the factors that control and determine the course of excited-state reactions in several different environments. We have studied both the influence of solvent identity and, in the newest work, composition and density in supercritical CO_2 mixtures including a co-solvent. In addition, we have explored the influence that initial vibrational excitation exerts in one prototypical system.

The work on stilbene and the biomimetic switch, NAIP, are descried in published articles and manuscripts are in preparation for the work on avobenzone and on salycilidene aniline in supercritical CO_2.

The Influence of Vibrational Excitation on the Photoisomerization of Electronically Excited trans-Stilbene in Solution. Kristin A. Briney, Leslie Herman, David S. Boucher, Adam D. Dunkelberger, and F. Fleming Crim, J. Phys. Chem. A **114**, 9788 (2010).

The Photoisomerization and Relaxation Dynamics of a Structurally Modified Biomimetic Photoswitch. Adam D. Dunkelberger, Ryan D. Kieda, Jae Yoon Shin, Riccardo Rossi Paccani, Stefania Fusi, Massimo Olivucci, and F. Fleming Crim, J. Phys. Chem. A **116**, 3527 (2012).