Structural Rearrangement Accompanying the Ultrafast Electrocyclization Reaction of a Photochromic Molecular Switch

Emanuele Pontecorvo,† Carino Ferrante,‡ Christopher G. Elles,*† and Tullio Scopigno*†§

†Dipartimento di Fisica, Università di Roma "Sapienza", P.le Aldo Moro 2, I-00185 Roma, Italy
‡Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States
§Centre for Life Nano Science IIT@Sapienza, Istituto Italiano di Tecnologia, I-00161 Roma, Italy

ABSTRACT: Probing the structural rearrangement of a model photochromic molecular switch provides a window on the fundamental dynamics of electrocyclization reactions. Taking advantage of resonance-enhanced femtosecond stimulated Raman scattering (FSRS) with a broadly tunable Raman excitation wavelength, we selectively probe the competing dynamics of both the reactive and nonreactive conformers of a diarylethene (DAE) derivative that are simultaneously present in solution. Measurements that preferentially probe the electrocyclization (ring-closing) reaction of the reactive species reveal an unexpectedly slow nuclear rearrangement, stretching to tens of picoseconds, in striking contrast with the prompt electronic dynamics in the formation of the closed-ring isomer. The different results from transient electronic and vibrational spectroscopies reflect the different aspects of the reaction that are probed by each technique, depending on whether one considers the electronic state of the molecule or the structural rearrangement of the nuclei. Using a different Raman excitation wavelength selectively probes the picosecond-scale intersystem crossing dynamics of the nonreactive conformer, revealing the vibrational spectra of the singlet and triplet excited states for the first time. The present study paves the way to a more complete understanding of the structural mechanisms accompanying the reversible photochromic switching process.

1. INTRODUCTION

Photoisomerization reactions that selectively change the structure of a molecule play a central role in optical data storage, molecular electronics, and many other technological applications. Some of the most popular compounds for these applications are photochromic diarylethene (DAE) derivatives that reversibly transform between open- and closed-ring isomers upon irradiation.1,2 Typically, UV excitation of the transparent open-ring isomer induces an efficient electrocyclization reaction that rearranges both the electronic and nuclear structure of the molecule, whereas irradiating the closed-ring isomer with visible light regenerates the original compound. In the closed-ring structure, the molecule develops a strong visible absorption band due to extended \( \pi \)-conjugation along the backbone of the nascent isomer. The formation of this electronic absorption band is very rapid, often lasting only a few hundred fs or less, which indicates that the electrocyclization reaction is complete on a similar time scale.3,4

Numerous time-resolved studies have probed the fundamental steps of the photoswitching process in DAE derivatives.3−8 However, most of the earlier studies monitor the dynamics using either transient electronic absorption or fluorescence techniques,3,4,9−12 both of which lack structural sensitivity. Very few experimental studies have directly reported on the molecular motions associated with ring closure. A stunning exception is the recent work by Miller and co-workers,6,10 who used time-resolved electron scattering to probe the structural dynamics of the ring-closing reaction of a photochromic molecular switch in a crystalline film on the fs time scale with atomic spatial resolution. Although the nuclear motions associated with the reaction coordinate were revealed in unprecedented detail, scattering techniques are not amenable to solution-phase studies, due to the inherent disorder of such systems.

Further complicating matters in solution, the open-ring isomer of most DAE compounds can adopt more than one conformational state, each with potentially different reaction pathways. For example, the molecule that we study here, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluoro-cyclopentene (DMPT-PFCP), exists in two primary conformations with roughly a 1:1 ratio and an interconversion time of around 90 ms at room temperature.13 The conformers differ in the relative orientation of the two phenylthiophene side groups. One species is a nonreactive conformer (NRC) with the side groups in a parallel orientation that prohibits the cyclization reaction, and the other is a reactive conformer (RC) with an antiparallel orientation of the side groups that prealigns the frontier orbitals for rapid electrocyclization.14 Competing signals from the reactive and nonreactive conformers significantly complicate the interpretation of transient absorption measurements. In
fact, the lack of a well-defined initial geometry for the open-ring isomer leads to multiple reaction pathways in solution, and therefore requires more selective methods for probing the electrocyclization dynamics than is possible using the broad, overlapping transient electronic absorption bands.

Time-resolved vibrational spectroscopy provides in principle the sensitivity to resolve the dynamics of multiple conformational states, as well as the desired structural information related to the electrocyclization reaction. Surprisingly, very few transient vibrational measurements have been reported for the ring-closing reaction of photochromic DAE molecular switches, leaving many unresolved questions about the fundamental dynamics of these popular molecules. In this paper, we use resonance-enhanced femtosecond stimulated Raman scattering (FSRS) to preferentially probe the ultrafast dynamics of the ring-closing reaction, even in the presence of competing reactions, and then contrast the electronic and nuclear dynamics of the electrocyclization reaction. Specifically, we probe the evolution of the vibrational spectrum following photoexcitation, while taking advantage of the wavelength tunability of our narrowband Raman probe to selectively monitor the response of the different molecular conformers that contribute to the transient signal. Electronic resonances provide a convenient means of selectively probing the different species via resonance enhancement of the transient Raman response. Our results provide important benchmarks for theoretical studies of DAE photoswitching reactions, as well as new insight on the nonadiabatic dynamics of electrocyclization.

2. EXPERIMENTAL METHODS

The experiment was performed in the Femtoscopy Laboratory at “Sapienza” University (Rome). Details of the femtosecond stimulated resonance Raman setup have been described elsewhere. Briefly, the setup is driven by an amplified Ti:sapphire laser (Coherent Legend Elite HE) producing 3.6 mJ, 35 fs pulses at 800 nm (450 cm⁻¹ bandwidth) and 1 kHz repetition rate. A portion of the laser fundamental is frequency tripled via successive stages of second harmonic generation and sum frequency generation to give <100 fs duration, 265 nm actinic pulses that are resonant with the UV absorption band of the closed-ring isomer of DMPT-PFCP. The evolution of the molecule is then probed via either transient electronic absorption or transient stimulated Raman scattering.

Widely tunable Raman pump pulses are an essential component of the resonance-enhanced femtosecond stimulated Raman scattering (FSRS) setup used here. The narrow bandwidth Raman pump pulses in the range 350–600 nm are generated from a commercial two-stage OPA (Light Conversion TOPAS-C) that produces tunable IR-visible pulses, followed by frequency doubling in a 25 mm BBO crystal. The final stage of second harmonic generation in the long BBO crystal is the key to generating narrow-band pulses via spectral compression. This technique takes advantage of the group velocity mismatch between the fundamental and second harmonic in the long BBO crystal to create few-ps duration pulses with typical bandwidths of ~15 cm⁻¹. Sharp edges in the temporal pulse profile that are characteristic of the spectral compression method can cause spectral ringing for vibrational bands associated with relatively long (>1–2 ps) dephasing times. We recently discussed these effects, and showed that a simple spectral filter significantly improves the line shape of Raman pump pulses obtained via spectral compression, although such pulse shaping was not necessary for the present experiment due to the short dephasing times (i.e., broad natural line widths) of the transitions observed here.

The femtosecond Raman probe is a white-light continuum generated by focusing the laser fundamental into a CaF₂ crystal that is continuously translated perpendicular to the beam to prevent damage. The transmitted WLC is collected through a spectrometer (Acton Spectra Pro 2500i) and dispersed on a CCD device (Princeton Instruments Pixis 100), which allows single shot acquisition. A synchronized chopper blocks alternating Raman pump pulses in order to obtain the Raman gain using successive probe pulses, and a second chopper blocks the actinic pump at 250 Hz in order to obtain Raman gain spectra with and without actinic excitation. We typically average 10⁵ laser shots to obtain the transient Raman spectrum at each delay time. Details of the baseline subtraction method are provided as Supporting Information.

The molecular switch (DMPT-PFCP) was purchased from TCI America, and dissolved in cyclohexane (Sigma-Aldrich, ≥ 99.9%) to a concentration that gives 10% transmission of the 265 nm actinic pulses through a 500 μm path length. The sample circulates through a flow-cell during the measurement in order to refresh the sample volume in the laser focus (~70 μm full width at half maximum) before every laser pulse. The Raman pump energy is typically set at 800 nJ per pulse, and the actinic pump at 2 μJ per pulse.

3. RESULTS AND DISCUSSION

Figure 1 shows the electronic absorption spectra of the open- and closed-ring isomers of DMPT-PFCP in cyclohexane.

Irradiating a solution of the transparent open-ring isomer with a 265 nm actinic laser pulse produces the transient electronic absorption spectra in Figure 2. The transient signal is initially dominated by two broad absorption bands centered near 400 and 580 nm, respectively, and then partially decays over several tens of picoseconds before reaching a stable state that lasts for more than a nanosecond. The steady-state spectrum beyond ~100 ps contains contributions from both the relaxed ground state of the closed-ring product and a long-lived excited state of the NRC, as illustrated by the dashed lines in the top panel of Figure 2.

The bottom panel of Figure 2 shows the time evolution of the transient absorption signal at two probe wavelengths. Importantly, the rapid rise of the electronic absorption at 560 nm, the maximum of the product absorption band, indicates that the electrocyclization reaction is complete within a few hundred fs of the initial excitation. The ps-scale decay of the...
Transient vibrational spectroscopy provides a more selective probe of the structural evolution of the system following UV excitation. For reference, Figure 3 shows the experimental and theoretical Raman spectra of both the open- and closed-ring isomers of DMPT-PFPC. The stimulated Raman spectra were obtained experimentally with a 370 nm Raman pump wavelength, which is resonant with the second absorption band of the molecule, although this effect is not included in the calculated spectrum.

The evolution of the 420 nm stimulated Raman spectrum is shown in Figure 4. As expected, the transient vibrational spectrum evolves on an ~23 ps time scale (bottom panel) that matches the ISC time obtained from the transient electronic absorption measurement. Specifically, some of the observed vibrational modes rise and others decay on the same time scale as the population dynamics between S1 and T1 of the NRC conformer. Remarkably, no significant variations of the transition frequencies are observed, implying negligible heating effects upon photoexcitation. The only vibrational band that does not evolve with the ISC time appears on a slightly longer time scale at ~1525 cm⁻¹. This outlier may be associated with a large-amplitude structural relaxation of the triplet excited state, similar to the behavior of the closed-ring product described below. Notably, we do not observe the characteristic Raman band of the closed-ring isomer at 1503 cm⁻¹, despite the fact that this molecule is electronically preresonant with the 420 nm Raman pump. The lack of Raman signal at 1503 cm⁻¹, even at the longest delay times, indicates that the resonance enhancement of the singlet and triplet states of the NRC dominates the transient vibrational spectrum at this pump wavelength. The open-ring isomer does not contribute to the 420 nm stimulated Raman spectrum because that molecule is a weak Raman scatterer that absorbs only below ~330 nm (see Figure 1).

We now explore other electronic resonances in order to resolve the dynamics associated with the reactive conformer of isomer. Additionally, the intensity of the ethylenic band may be further enhanced due to the Raman pump being resonant with the second absorption band of the molecule, although this effect is not included in the calculated spectrum.
The frequency of this mode is similar to the 1503 cm$^{-1}$ mode sensitive to the degree of conjugation along the backbone of the molecule, because delocalization of the π-electrons increases the polarizability, and therefore also the Raman cross section. In other words, although the high-frequency 1503 cm$^{-1}$ vibration is not directly involved in ring closure, this mode provides a sensitive probe of the structural dynamics of the electrocyclization reaction. The delayed appearance of the intense 1503 cm$^{-1}$ mode suggests that the molecule does not reach the equilibrium ground state of the closed-ring product for several tens of ps.

Figure 5 shows the evolution of the transient stimulated Raman spectrum in the 1400–1600 cm$^{-1}$ region in finer detail. Remarkably, for time delays <5 ps, the largest contribution to the transient Raman spectrum in this range is located around 1485 cm$^{-1}$. The frequency of this mode is similar to the 1487 cm$^{-1}$ mode that we assigned to the S$_1$ state of the NRC in the 420 nm transient Raman spectrum (Figure 4). However, we do not observe a comparable band near 1571 cm$^{-1}$, which suggests that the 1485 cm$^{-1}$ vibration in the 560 nm transient Raman spectrum is not due to the NRC. An alternative explanation is that the weak 1485 cm$^{-1}$ mode is a signature of the hot ground state of the closed-ring product, such as an ethylenic stretch that is shifted to lower energy and has reduced intensity compared with the relaxed molecule. The relatively weak contribution disappears at longer delay times, when this region of the spectrum is dominated instead by the strong ethylenic band of the closed-ring product at 1503 cm$^{-1}$.

Interestingly, even at long delay times, the Raman band at ∼1503 cm$^{-1}$ cannot be modeled by a single mode, because of an additional, broad contribution at slightly lower energy than the dominant narrow feature. Figure 6B shows the decomposition of the Raman peak at 490 ps into a sum of two Gaussian bands, one centered at 1503 cm$^{-1}$ and the other at slightly lower frequency. The lower-frequency 1485 cm$^{-1}$ mode does not contribute at this long delay time.

Given the different bands observed, we model the evolution of the vibrational spectrum in this region as a sum of three Gaussian modes, one to account for the peak related to the hot photoproduct at 1485 cm$^{-1}$ and the other two to reproduce the two contributions that appear at longer delay times. The only free parameters used to fit the Raman spectrum at each time delay are the peak intensities of each band and the frequency shift of the two contributions from the closed-ring isomer relative to the long-time limit. The best fit of the transient...
bands. The solid line is a biexponential sum of the two contributions from the relaxed closed-ring isomer. (E) Time-dependent frequency shift of the closed-ring isomer, shifts exponentially on a time scale of 18 ps, while the band intensity increases on a time scale that is slower by at least a factor of 2 (Figure 6D,E). Similarly, the broad band at 1485 cm$^{-1}$, and red and cyan markers are the narrow and broad frequency-shifted bands of the closed-ring isomer, respectively. The lines are exponential fits, except the magenta line, which is the sum of the two contributions from the relaxed closed-ring isomer bands. (E) Time-dependent frequency shift of the closed-ring isomer bands. The solid line is a biexponential fit.

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

A description of the baseline subtraction method for obtaining transient stimulated Raman spectra with resonant Raman pump wavelengths is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: elles@ku.edu.
*E-mail: tullio.scopigno@phys.uniroma1.it.

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

A description of the baseline subtraction method for obtaining transient stimulated Raman spectra with resonant Raman pump wavelengths is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: elles@ku.edu.
*E-mail: tullio.scopigno@phys.uniroma1.it.

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

A description of the baseline subtraction method for obtaining transient stimulated Raman spectra with resonant Raman pump wavelengths is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: elles@ku.edu.
*E-mail: tullio.scopigno@phys.uniroma1.it.

Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The authors thank Dr. Igor L. Zheldakov for providing computational Raman spectra and Timothy J. Quincy for the transient electronic absorption spectrum in Figure 2. C.G.E. is grateful for the hospitality and support while at the Università di Roma “La Sapienza” as a Visiting Professor, and for additional support from a National Science Foundation CAREER Award (NSF-1151555). E.P., C.F., and T.S. have received funding from the European Research Council under the European Community’s Seventh Framework Program (FP7/2007–2013)/ERC grant agreement No. 207916.

REFERENCES


