

Mechanisms of Molecular Response in the Optimal Control of Photoisomerization

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(Received 20 June 2006; published 20 December 2006)

We report on adaptive feedback control of photoinduced barrierless isomerization of 1,1'-diethyl-2,2'-cyanine in solution. We compare the effect of different fitness parameters and show that optimal control of the absolute yield of isomerization (photoisomer concentration versus excitation photons) can be achieved, while the relative isomerization yield (photoisomer concentration versus number of relaxed excited-state molecules) is unaffected by adaptive feedback control. The temporal structure of the optimized excitation pulses allows one to draw clear mechanistic conclusions showing the critical importance of coherent nuclear motion for the control of isomerization.

DOI: 10.1103/PhysRevLett.97.258301

PACS numbers: 82.50.Nd, 33.20.Tp, 82.30.Qt, 82.50.Nd

Ultrafast, photoinduced isomerization has attracted much attention because of its importance in biology and chemistry [1–3]. Recently, theoretical studies [4,5] suggested the possibility of using adaptive feedback control to experimentally influence the quantum yield of isomerization in cyanines, a paradigm class of molecules to study photoinduced isomerization [6–8]. In an adaptive feedback control experiment, an automated learning loop is used to obtain a coherent light field best suited to solve the control task in a self-consistent manner [9–11] without any *a priori* knowledge about the molecular Hamiltonian. However, this approach imposes the central challenge to extract the control mechanism from the optimized electric field [12], certainly a nontrivial task.

A first experiment controlling photoinduced isomerization was reported by Gerber and co-workers [13]. The latter work and a related theoretical approach by Hoki and Brumer [14] were restrained to an interpretation of the experimental data in the Bagchi, Fleming, Oxtoby (BFO) model of isomerization [15]. This “classical” one-dimensional model considers only the dominant isomerization coordinate, i.e., torsion angle reflecting bond twisting. Therefore, the discussions in [13,14] rely on a simplified model compared to recent theoretical work [4,5,16], which show the importance of the multidimensionality of the excited-state potential-energy surface (PES) for optimal control of the photophysics of cyanines. As a result of the various levels of approximation when considering the excited-state PES, a variety of explanations of the underlying isomerization mechanisms has been considered. Theoretical studies suggest that altering the momentum distribution within the initial photoexcited wave packet will allow one to control isomerization dynamics of cyanines [5], while in [13] the experiment is explained in terms of higher lying S_n states being populated by sequential absorptions. Optimizing photoexcitation under strongly dissipative conditions is suggested as being responsible for the observed pulse shapes in [14]. Finally, other calculations point toward the existence of

two different relaxation pathways on the excited-state PES, whose interference might open a doorway for control of isomerization [16].

In this Letter, results of applying adaptive feedback control to photoisomerization in the liquid phase are presented. We chose 1,1'-diethyl-2,2'-cyanine (1122C), a molecule well characterized, for this study. Several investigations on 1122C indicate a barrierless excited-state isomerization [16,17]. In this study a mechanism of controlling a fast chemical reaction in a strongly interacting environment is suggested and mechanistic details of excited-state isomerization in relation to earlier work [5,13,14,16] are revealed.

1122C was purchased from Sigma Aldrich and used without further purification. It was dissolved in methanol to yield optical densities of about 0.3 at the excitation wavelength. Independently wavelength-tunable laser pulses with pulse durations of typically 30 fs were generated for the probe and the pump light, respectively. Pulse shaping of the excitation pulses was achieved by phase control using a 4*f*-zero dispersion compressor combined with a liquid-crystal array based pulse shaper and a self-learning adaptive feedback loop [18]. The pump pulse was centered at 495 nm, while the probe pulse was set to 550 nm.

The probe wavelength falls into a spectral region where contributions from ground-state bleach, stimulated emission, and absorption of the photoisomer are observed [17]. Immediately after photoexcitation at 495 nm a short-lived negative absorption change is visible, attributed to stimulated emission from initially hot excited-state molecules [Fig. 1(c)]. After about 200 fs the hot emission contribution has disappeared leaving relaxed excited-state population and the remaining negative amplitude in the transient kinetics is explained by ground-state bleach, turning into absorption of the *cis*-photoisomer. The disappearance of the isomer absorption because of the thermally driven back reaction of *cis*- into *trans*-cyanine molecules takes place on a nanosecond time scale. Thus, controlling the absolute

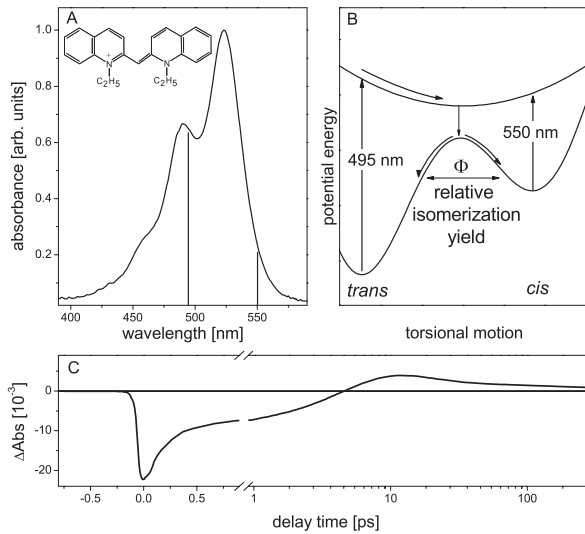


FIG. 1. (a) Chemical structure of *trans*-1122C and absorption spectrum. Solid lines indicate wavelengths used in the experiments. (b) Schematic one-dimensional representation of barrierless excited-state isomerization. The reaction coordinate represents torsional motion around the isomerizing bond. (c) Transient absorption changes recorded after photoexcitation with a transform limited pulse.

value of the ratio of ΔAbs at two different delay times [19] corresponding to ground-state bleach (at 1 ps) and photoisomer absorption (at 15 ps) will allow for optimization of the relative quantum yield of isomerization defined as the ratio of the number of *cis*- and the number of relaxed photoexcited *trans*-molecules. The latter quantity in turn is proportional to the ground-state bleach signal. This choice of target avoids the problems of the fitness chosen in the first control study of isomerization [13,14], which may lead to complications because of absorption contributions from different ground-state species as indicated in [16]. However, using the ratio $\Delta\text{Abs}(1 \text{ ps})/\Delta\text{Abs}(15 \text{ ps})$ as fitness parameter we were not able to obtain any control of the relative isomerization quantum yield (Fig. 2) [14,20].

Following Brumer's idea [14] we changed the target parameter to control the absolute quantum yield of isomerization, i.e., the number of *cis*-isomers produced versus the overall number of photons in the excitation pulse [21]. This fitness allowed the adaptive feedback algorithm to solve the experimentally imposed task and to find optimized laser pulse shapes that minimize (maximize) the target value (Fig. 2). When subjected to adaptive feedback control, the absolute isomerization yield can be reduced and enhanced significantly.

Noteworthy, the ΔAbs transients recorded after excitation with the complex structured optimized pulses for minimization and maximization exhibit the crossover between ground-state bleach and isomer absorption at identical delay times [Fig. 3(c)]. This strongly suggests that the

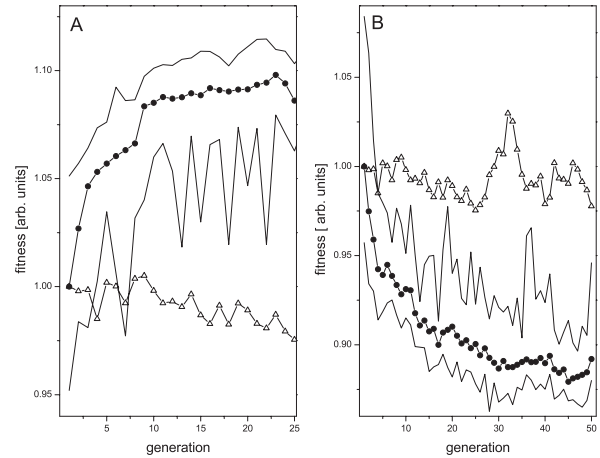


FIG. 2. Evolution of the fitness parameter for maximization (a) and minimization (b) of absolute quantum yield of isomerization. Solid circles represent the average fitness and lines the best or worst fitness per generation. The triangles refer to the attempt to optimize the relative quantum yield representing the noise level of our control setup.

shaped excitation pulses do not lead to different reaction pathways on the excited-state PES that interfere to obtain the desired control [16]. For such a situation, we would anticipate drastically altered dynamics and kinetics of the system. This finding is further supported by displaying the ΔAbs kinetics normalized to the *cis*-isomer absorption at 15 ps, the delay time used in the control experiment [inset Fig. 3(c)]. The transients are identical for delay times longer than a few picoseconds. Thus, any relevant dynamics used to achieve the control task is constrained to a small

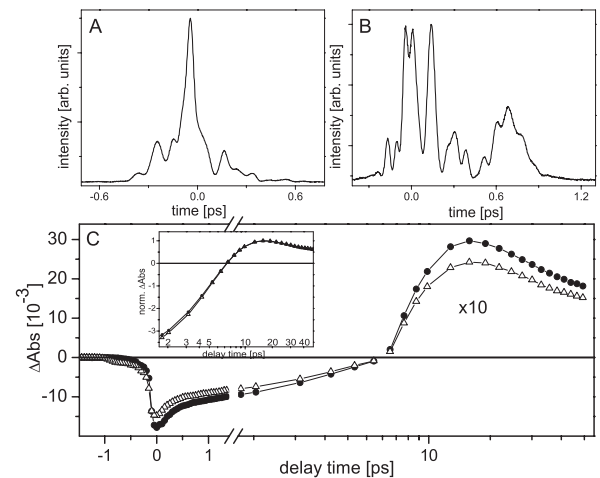


FIG. 3. Intensity cross-correlations of optimized pulses are shown for (a) maximization and (b) minimization of the absolute yield of isomerization. (c) Absorption changes recorded for optimized pulses. Solid circles and triangles refer to the pulses shown in (a) and (b), respectively. Inset: Transients shown in (c) are displayed normalized to the photoinduced absorption at 15 ps.

time window after interaction of the system with the pump pulse. The molecules being left on the excited-state PES forming the relaxed excited-state population relax down to the ground state along identical paths resulting in the unaltered kinetics observed for long delay times.

The ability to control the number of photoisomers versus number of photons in the excitation pulse in concert with the failure to control the photoisomer formation versus the number of relaxed excited-state molecules reveals details about the achieved control. Although, both fitnesses would lead to an increase of one ground-state isomer at the expense of the other, the different success in employing them in an optimal control scheme shows that the decisive moment of the optimal control does not happen in the vicinity of the bottom of the excited-state PES. Instead, control is achieved only when higher lying parts of the excited-state PES are accessed.

The optimized laser fields are characterized by sum-frequency harmonic generation XFROG and intensity cross correlation with the transform limited probe pulse. We ensured that the essential information of the XFROG data is reflected in the temporal structure of the cross correlations (Fig. 3). To gain further insight into the processes underlying control and to correlate the experimental findings with the intramolecular degrees of freedom, Fourier transformations of the temporal pump-pulse structures were performed (Fig. 4). As can be seen, oscillations of the temporal envelope corresponding to wave numbers up to about 600 cm^{-1} are found, correlating with the 500 cm^{-1} spectral full width half maximum of the transform limited pump pulse. In literature, Raman modes of pseudocyanine in the wave number region up to 500 cm^{-1} are assigned to vibrations involving the methine bridge and adjacent C-N bonds [22]. It is interesting to compare the frequency spectrum of the pulse trains resulting from

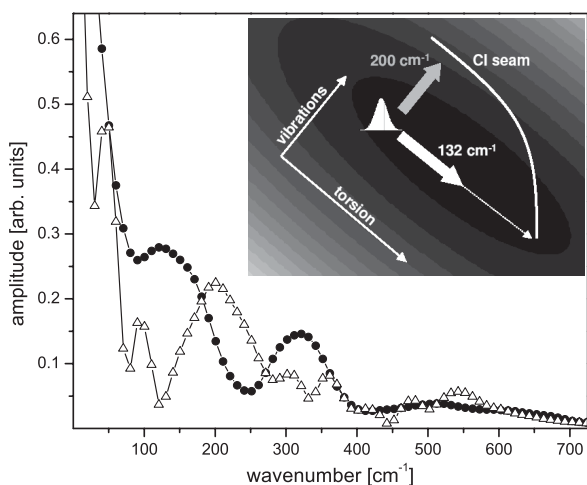


FIG. 4. Amplitudes of Fourier transformations of the optimized pulses. Solid circles (open triangles) refer to the maximization (minimization) pulse displayed in Fig. 3(a) (b). Inset: schematic depiction of suggested control mechanism.

minimizing and maximizing the absolute quantum yield. Striking differences can be found: The pulse train maximizing photoisomer absorption exhibits pronounced maxima at 130 and 320 cm^{-1} , coinciding with minima at 124 and 330 cm^{-1} in the spectrum of the minimization pulse. The Fourier transform of the latter displays a strong contribution at 200 cm^{-1} accompanied by minor peaks at 100 , 300 , and 360 cm^{-1} . The Fourier transforms of both pulses contain modes with wave numbers below 100 cm^{-1} and minor contributions at $500\text{--}600\text{ cm}^{-1}$ [23]. As they are present in both minimization and maximization pulses they do not seem to influence the photoisomerization significantly. These findings allow us to draw distinct mechanistic conclusions and correlate our experimental results with discrete mechanisms to obtain a control over the photoisomerization. The proposed mechanism is intrinsically related to the internal vibrational degrees of freedom of 1122C. The results presented here are in line with computational and experimental evidence for an extension of the classical BFO model of barrierless isomerization [15] taking into account the multidimensionality of the excited-state PES [4,5,16]. It was shown that independent of solvent viscosity, vibrational modes coupled to the electronic transition are preserved for the time scale of diffusive downhill motion along the torsion coordinate [24]. Thus, the different spectral compositions of the pulses obtained from adaptive feedback control can be rationalized along the lines suggested in [5]. There it is argued that an elongated conical intersection (CI) seam extends from the bottom of the excited-state PES to locations close to the Franck-Condon point while it is displaced from the one-dimensional bond-twisting pathway. By experimentally controlling the momentum composition of the initially prepared wave packet the location on the excited-state PES, where the wave packet will encounter the CI seam, can be controlled. Enhancing the motion of the wave packet orthogonal to the bond-twisting coordinate the excited-state population will pass through the CI some distance from the minimum of the PES on the side of the *trans*-isomer, thereby reducing the number of *cis*-isomers formed. Favoring relaxation along the torsional motion coordinate to the sink region leads to an increased formation of *cis*-molecules [5]. Within this argumentation it can be concluded that the 200 cm^{-1} mode, predominantly visible in the pulse minimizing photoisomer production, moves the excited-state population toward the CI seam on the *trans*-side of the ground-state potential. Hence, populating this mode results in a decrease of absolute isomerization yield. On the other hand, excitation of the 132 cm^{-1} mode results in enhancement of the downhill motion along the isomerization coordinate, causing the system to reach the CI close to the bottom of the excited-state potential and thus to increase the absolute quantum yield of isomerization [5]. The exact nature of the modes involved in the suggested control mechanism as schemati-

cally depicted in Fig. 4 remains unsolved at the moment and is a subject of recent investigations [23]. The normalized transients being superimposable for delay times longer than the pulse duration indicates that motion along other orthogonal coordinates does not push molecules toward the extended CI seam before relaxing to the bottom of the excited-state PES. Thus, the reaction kinetics after the concerted pump-pulse interaction will be dominated by torsional motion, leaving the observed kinetics unaffected.

Another possibility to account for the reduction of the absolute isomerization quantum yield might be pump-dump with the temporal structure of the excitation pulse linking individual pump and dump events to the internal clock provided by the vibrations of 1122C. Though it is not obvious how to account for the observed increase of isomerization quantum yield in this framework, we cannot exclude this possibility based on our experimental results. Less efficient population of the excited state by the minimization pulse can be excluded as only phase shaping is used, and thus the integrated field amplitude and spectral composition of the pulses remain unchanged.

In conclusion, we report on adaptive feedback control of the photoinduced isomerization of 1,1'-diethyl-2,2'-cyanine in solution. Significant control of the absolute quantum yield of isomerization could be achieved, i.e., control of the number of photoisomers per incident photon, while we were not able to optimize the production of photoisomers versus the number of relaxed excited-state molecules measured at delay times longer than the pump-pulse duration. The optimized pulses exhibit a complex temporal structure, which can be related to the intramolecular degrees of freedom of 1122C. These results indicate the conversion of photoexcited *trans*-molecules back into the *trans*-ground state by immediately directing the initial wave packet toward an extended CI seam within the pump-pulse duration [5]. On the other hand, changing the momentum composition of the wave packet results in a reduced population flow through this immediate deactivation channel and correspondingly to an enhanced relaxation into the bottom of the excited-state PES. Having relaxed to the sink region the molecules pass through the CI resulting in an increase of photoisomer formation. It is proven that vibrational modes orthogonal to the dominant torsional motion have to be considered in understanding the optimal control of isomerization, thus showing the validity of recent theoretical approaches [4,5,16] for barrierless isomerization.

We highly acknowledge Dr. J. A. Organero's help with the experimental setup and many stimulating discussions with Professor Villy Sundström. This work was supported by the Knut and Alice Wallenberg Foundation,

the Crafoord Foundation, and the Swedish Science Foundation.

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- [1] R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, *Science* **254**, 412 (1991).
- [2] P. Kakura, D. W. McCamant, S. Yoon, D. B. Wand-schneider, and R. A. Mathies, *Science* **310**, 1006 (2005).
- [3] F. Gai, K. C. Hansson, J. C. McDonald, and P. A. Anfinrud, *Science* **279**, 1886 (1998).
- [4] A. Sanchez-Galvez, P. Hunt, M. A. Robb, M. Olivucci, T. Vreven, and H. Schlegel, *J. Am. Chem. Soc.* **122**, 2911 (2000).
- [5] P. A. Hunt and M. A. Robb, *J. Am. Chem. Soc.* **127**, 5720 (2005).
- [6] A. Yartsev, J. Alvarez, U. Aberg, and V. Sundström, *Chem. Phys. Lett.* **243**, 281 (1995).
- [7] J. Alvarez, A. Yartsev, U. Aberg, E. Akesson, and V. Sundström, *J. Phys. Chem. B* **102**, 7651 (1998).
- [8] G. H. Xu and G. R. Fleming, *J. Phys. Chem. A* **105**, 10 187 (2001).
- [9] R. S. Judson and H. Rabitz, *Phys. Rev. Lett.* **68**, 1500 (1992).
- [10] A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, and G. Gerber, *Science* **282**, 919 (1998).
- [11] J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, and M. Motzkus, *Nature (London)* **417**, 533 (2002).
- [12] C. Daniel, J. Full, L. Gonzalez, C. Lupulescu, J. Manz, A. Merli, S. Vajda, and L. Wöste, *Science* **299**, 536 (2003).
- [13] G. Vogt, G. Krampert, P. Niklaus, P. Nuernberger, and G. Gerber, *Phys. Rev. Lett.* **94**, 068305 (2005).
- [14] K. Hoki and P. Brumer, *Phys. Rev. Lett.* **95**, 168305 (2005).
- [15] B. Bagchi, G. R. Fleming, and D. W. Oxtoby, *J. Chem. Phys.* **78**, 7375 (1983).
- [16] F. Improta and F. Santoro, *J. Chem. Theory Comput.* **1**, 215 (2005).
- [17] B. Dietzek, A. Yartsev, and A. N. Tarnovsky, *J. Phys. Chem. B* (to be published).
- [18] B. Brüggemann, J. A. Organero, T. Pascher, T. Pullerits, and A. Yartsev, *Phys. Rev. Lett.* **97**, 208301 (2006).
- [19] To reduce excitation-related noise, Δ Abs signals are taken at the same time by means of two independently delayed probe pulses.
- [20] It has been carefully verified that various experimental runs yielded the same, negative, result.
- [21] Measured by the reflection of the pump light off the focusing lens.
- [22] C. Guo, M. Aydin, G. R. Zhu, and D. L. Akins, *J. Phys. Chem. B* **106**, 5447 (2002).
- [23] P. Persson *et al.* (unpublished).
- [24] B. Dietzek, N. Christensson, T. Pascher, T. Pullerits, and A. Yartsev (to be published).