

Tracking Ultrafast Excited-State Bond-Twisting Motion in Solution Close to the Franck–Condon Point

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Applying optimal control to photoinduced trans–cis isomerization in condensed phase, the dynamics of bond-twisting motion of 1,1'-diethyl-4,4'-cyanine in methanol and propanol is revealed. The shape of the optimized pulse resulting from minimization of the photoisomer formation can be directly related to the initial excited-state dynamics in close proximity to the Franck–Condon point. The solvent viscosity-dependent ultrafast wavepacket motion is reflected in the prominent down-chirp of the optimized pulses and reveals a detailed picture of the control mechanism: The reduction of the isomer production is achieved by most efficient dumping of excited population back to the trans ground state. In the higher-viscosity solvent, propanol, wavelength-dependent oscillatory features are superimposed to the overall chirp structure pointing to the importance of excited-state vibrational coherences for the dumping process.

Introduction

Light-induced cis–trans isomerization is a fundamental reaction in chemistry and biology; it is of crucial importance in vision^{1,2} and in the photoreception of plants and some bacteria.³ The growing interest in these biological systems lately triggered both detailed experimental and advanced ab initio theoretical investigations of the potential energy surfaces of cyanine dyes^{4–8}—paradigm models for ultrafast excited-state isomerization.^{9,10} Very recently, adaptive feedback control^{11–17} was applied to influence the outcome of the photoinduced isomerization reaction of cyanines^{18–20} and the retinal chromophore in bacteriorhodopsin.²¹ These studies show the possibility of experimentally influencing the quantum yield of an isomerization reaction, thus opening the doorway to a more detailed understanding of the special design of natural photoreceptors.³

In this study, we apply adaptive feedback control as a spectroscopic tool to monitor the ultrafast excited-state wavepacket motion in 1,1'-diethyl-4,4'-cyanine (1144C) in solutions. Instead of aiming to influence the outcome of the chemical reaction,^{12,14,18,20,21} optimal control intrapulse pump-dump is used to reveal details of the ultrafast light-induced bond-twisting motion near the Franck–Condon point, i.e., a region of the potential energy surface, in which it is difficult to access the ultrafast dynamics by means of conventional time-resolved spectroscopy. A systematic and parametrized control of the chirp to induce an intrapulse pump-dump process was employed in earlier work.^{22,23} However, this approach does not allow for the flexibility of an adaptive feedback control experiment. Optimal control on the other hand in concert with the potential of a self-learning adaptive feedback loop offers two conceptual advantages above parametrized control of the pulse parameters: First is the capability of generating more complex pulse-trains (as discussed below) that might enhance dumping beyond the level

accessible by imposing single-parameter controlled chirp. Second, adaptive feedback control provides a more general solution to the task of influencing the molecular dynamics. While parametrized control imposes a specific reaction of the system under study, adaptive feedback control expresses the information intrinsic to the system and crucial for the reaction dynamics. Thereby it reveals more detailed information on the excited-state relaxation in complex reactive systems.^{13,14,16,20,21}

The ultrafast excited-state isomerization reaction of 1144C has been studied extensively using conventional femtosecond transient absorption,^{24–27} fluorescence up-conversion²⁸ and three-pulse photon-echo peak-shift spectroscopy.²⁹ A schematic of the potential-energy curves conventionally invoked to account for the experimental findings is depicted in Figure 1. Upon optical excitation of the thermally stable trans form to the S₁-state the initially prepared wavepacket relaxes to the bottom of the excited-state potential corresponding to a 90°-twist of the quinoline end-groups (process 1 – Figure 1B). During the downhill relaxation the excited molecules transiently populate geometrical structures corresponding to successively decreased energetic separations between the S₀ and S₁ state. Thus, the motion toward the 90°-twist geometry in 1144C and related systems can be mapped onto the spectral-temporal evolution of fluorescence²⁸ or stimulated emission.⁵ At the bottom of the excited state the derivative of the potential with respect to the reaction coordinate is zero and stochastic Brownian bond-twisting motion is predicted by theory (process 2).^{30,31} When encountering the sink position, the system undergoes a radiationless transition back to the S₀-state (process 3),^{30,31} where torsion motion leads to the formation of the cis isomer and refilling of the trans ground state (process 4). The photoisomer, i.e., cis form of 1144C, is found to absorb slightly red-shifted compared to the trans form that determines the differential absorption spectrum at long delay times.²⁵ The characteristic time-scales for ground-state recovery of 1144C in methanol and propanol was reported to be approximately 1 and 4 ps, respectively.²⁵

The excited-state relaxation in 1144C (Figure 1B) can be mapped onto the spectral-temporal evolution of the system's

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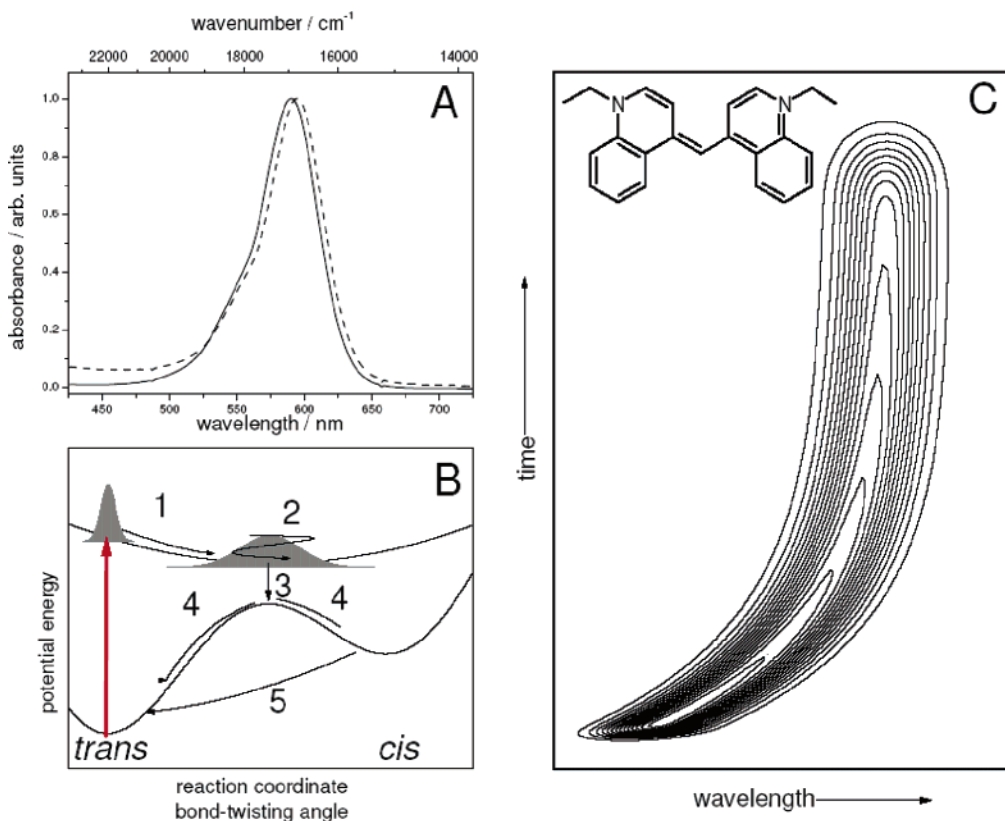


Figure 1. Steady-state absorption spectrum of 1144C in methanol (A). Schematic one-dimensional model to account for photoinduced processes (B). For details, see text. Chemical structure of 1,1'-diethyl-4,4'-cyanine and schematic two-dimensional plot of emission wavelength vs time, while the system evolves on the excited-state potential (C).

fluorescence resulting in an emission dynamics as schematically shown in Figure 1C. Upon photoexcitation the system starts to relax to the bottom of the excited-state potential-energy surface (ES-PES). The excited-state bond twisting results in increasingly red-shifted emission as the energetic difference between the excited- and the ground-state potential decreases with increasing bond-twisting angles.⁵ The Stokes shift levels off, when the system reaches the flat part of the potential. During Brownian, random torsion motion, the shape of the excited-state wavepacket; i.e., of the torsion-angle distribution, remains unchanged,^{30,31} and hence the shape of the emission spectrum is conserved. Finally, molecules undergo radiationless transitions back to the ground state resulting in disappearance of the emission. The large amplitude torsion motion has been observed in 1144C by means of fluorescence up-conversion.²⁸ An overall picture of the relaxation on the S₁-potential energy surface was obtained and the barrierless nature of the photoinduced isomerization was directly visualized.²⁸ However, in ref 28 the recorded fluorescence was Stokes-shifted more than 2700 cm⁻¹ from the excitation wavelength. Therefore, it followed the photoreaction far from the Franck–Condon point and thus far from the initially photoexcited torsion-angle distribution.

In this work we obtain direct insight into the solvent dependence of the excited-state bond-twisting motion of 1144C near the Franck–Condon point. The data presented reveal the reaction dynamics at small torsion angles changes from the trans geometry forming the thermodynamically stable ground-state isomer. This was achieved by using the tools provided by adaptive feedback control.^{11–21} The obtained optimized pulse-shapes disclose detailed information about ultrafast excited-state reactions.^{13,14,20,21} The experimentally imposed task to minimize the formation of 1144C photoisomers results in an optimized pump-pulse shape that exhibit clear signatures of intrapulse

pump-dump process.^{22,23,32,33} As a result of the dumping the number of excited-state molecules at the bottom of the excited-state potential is reduced, which directly translates into a reduced yield of photoisomers.²⁰ The optimized pulse-shapes reflect the stimulated emission properties of the system (Figure 1C), which in turn represent the excited-state dynamics of 1144C. Thus, analysis of the obtained pulse shapes yields detailed insight into the bond-twisting dynamics at small torsion angles and thus close to the Franck–Condon point.

Experimental Section

The laser system and the experimental setup used for the optimal control experiments have been described elsewhere.^{34,35} In short, the pulses of an amplified fiber oscillator (Clark, CPA 2001) are used to pump tunable noncollinear optical parametric amplifiers (TOPASwhite, Light Conversion, and NOPA, Clark) at a repetition rate of 1 kHz to generate the pump and probe pulses used in the experiment. The pump pulse was centered at 600 nm, and thus about 220 cm⁻¹ red-shifted with respect to the maximum of the absorption spectrum. Its spectral width (fwhm) was 670 cm⁻¹. The probe was tuned to the cis isomer absorption at 675 nm. At this wavelength, the appearance of the cis isomer is probed at long delay times, while at short delays contributions from ground state bleaching and stimulated emission are observed.²⁵ The experimental response function was measured to be 50 fs at the sample position by means of sum-frequency generation in a 30 μm BBO crystal. Phase shaping of the excitation pulses was obtained by utilizing a 4f-zero dispersion compressor combined with liquid-crystal array placed in the Fourier plane of the compressor.³⁶ A self-learning adaptive feedback loop was employed to optimize the excitation pulses. Characterization of the resultant pulse-shapes was done

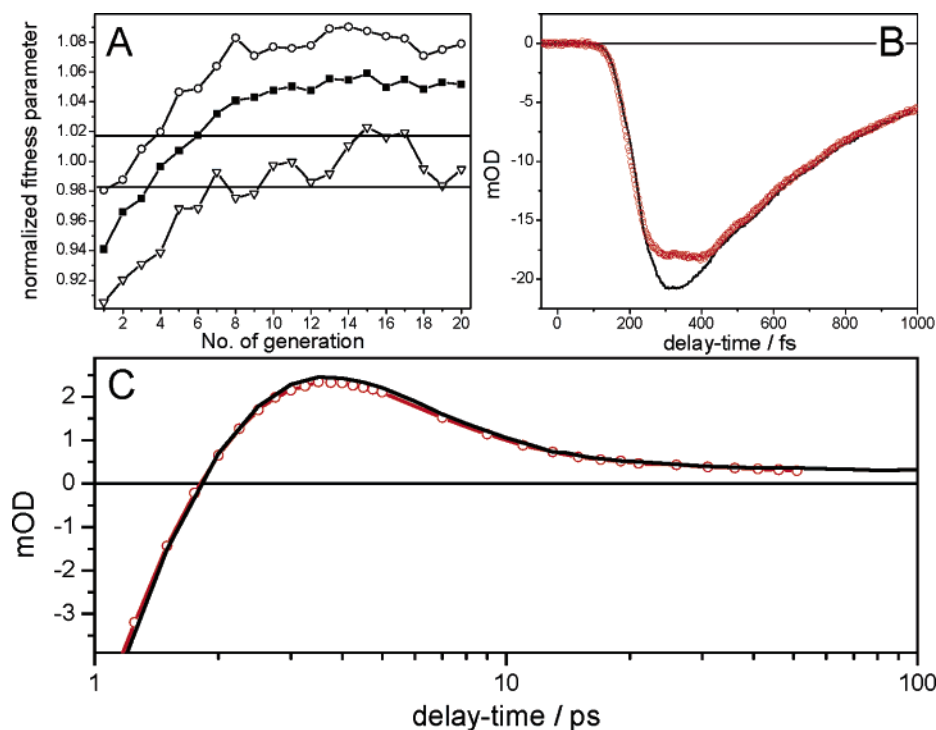


Figure 2. Evolution of fitness parameter for minimization of photoisomer production of 1144C in methanol (A). Solid squares represent the average fitness of the 50 individuals per generation, while open circles and triangles refer to the best and the worst pulse in a particular generation, respectively. The horizontal lines indicate the range of the normalized fitness parameter obtained with transform-limited pump pulses. Transient absorption kinetics recorded with close-to transform-limited reference and optimized pump pulse (B, short delay times reflecting ground state bleach and stimulated emission; C, long delay times reflecting excited-state absorption and photoisomer absorption).

using sum-frequency generation cross-correlated frequency-resolved optical gating (xFROG) in a 30 μm BBO crystal at the sample position. As xFROGs were recorded with the optimized pump- and transform-limited probe pulses, the spectral-temporal features of the xFROG traces directly reflect changes in the pump pulse.³⁷

1144C was used as provided by *SigmaAldrich* and dissolved in methanol and propanol of spectroscopic grade to yield an optical density of typically 0.5 at 600 nm in a 1-mm quartz cuvette. Recording absorption spectra, the integrity of the sample was ensured.

Results and Discussions

The absorption spectrum of 1144C in methanol and propanol is shown in Figure 1A. It exhibits characteristic features of the absorption of a small cyanine dye.¹⁰ The main transition is centered at 591 nm (methanol) and found to be red-shifted by 1 nm, when using propanol to dissolve the sample.³⁸ Besides the main transition, a vibronic shoulder is observed at 545 nm.

Following our objective to monitor the ultrafast initial bond-twisting motion of photoexcited 1144C, we pursued the idea of utilizing an intrapulse pump-dump scheme.^{22,23,32,33} Hence, we imposed the task to minimize the number of *cis* isomers produced in the very fast photoreaction to the self-learning adaptive feedback loop.^{11,12,16,17} As the overall excited-state lifetime of 1144C in methanol is on the order of only 1 ps,²⁵ the time window in which the adaptive feedback loop can access the excited-state dynamics and thus influence the reaction outcome is very short compared to studies on related systems.^{18,20} Hence, the choice of fitness is likely to translate into a reduced number of molecules reaching the bottom of the excited-state potential and therefore most efficient dumping of the initial photoexcited population.^{22,23,33} The number of the produced *cis* isomers should be proportional to the differential

absorption signal at delay times after spectral evolution has come to halt. In the experiments presented here, the number of *cis* isomers formed in the reaction is monitored at 10 ps (30 ps) for methanol (propanol) as solvent and thus for both solvents at a time, at which the excited-state has decayed.

Figure 2 displays the evolution of the parameters of the control experiment performed for methanol as solvent. Panel A shows the evolution of the fitness, which was defined as the integrated number of photons in the excitation pulse divided by the differential absorption signal recorded at 675 nm and at a delay time of 10 ps. Thereby it is ensured, that fluctuations in the pump intensity do not give rise to a dominant noise contribution in the experimental task. The fitness rises during the first generations before finally leveling off at a constant level after about 12 generations. This indicates that the adaptive feedback loop quickly succeeded in finding an optimized solution to the problem of minimizing the number of isomers produced per incident photon. Panel B confirms this result by displaying the transient absorption kinetic recorded with the optimized and the transform limited reference pulse. There one can see already a decrease of the initial negative differential absorption signal, which is due to ground-state bleach and stimulated emission. The positive differential absorption signal for long delay times is accounted for by *cis* isomer absorption only.²⁵ A similar experimental trend was observed, when a minimization of the differential absorption signal, reflecting the number of photoisomers, of 1144C in propanol (data not shown) was performed.

In order to correlate the effect of the optimized pulse to dynamical processes in the photoexcited molecules, Figure 3 presents the results of representative xFROG measurements performed with the optimized pump- and transform-limited probe pulses. The reproducibility of the results has been confirmed in at least four independent experiments.³⁹ While

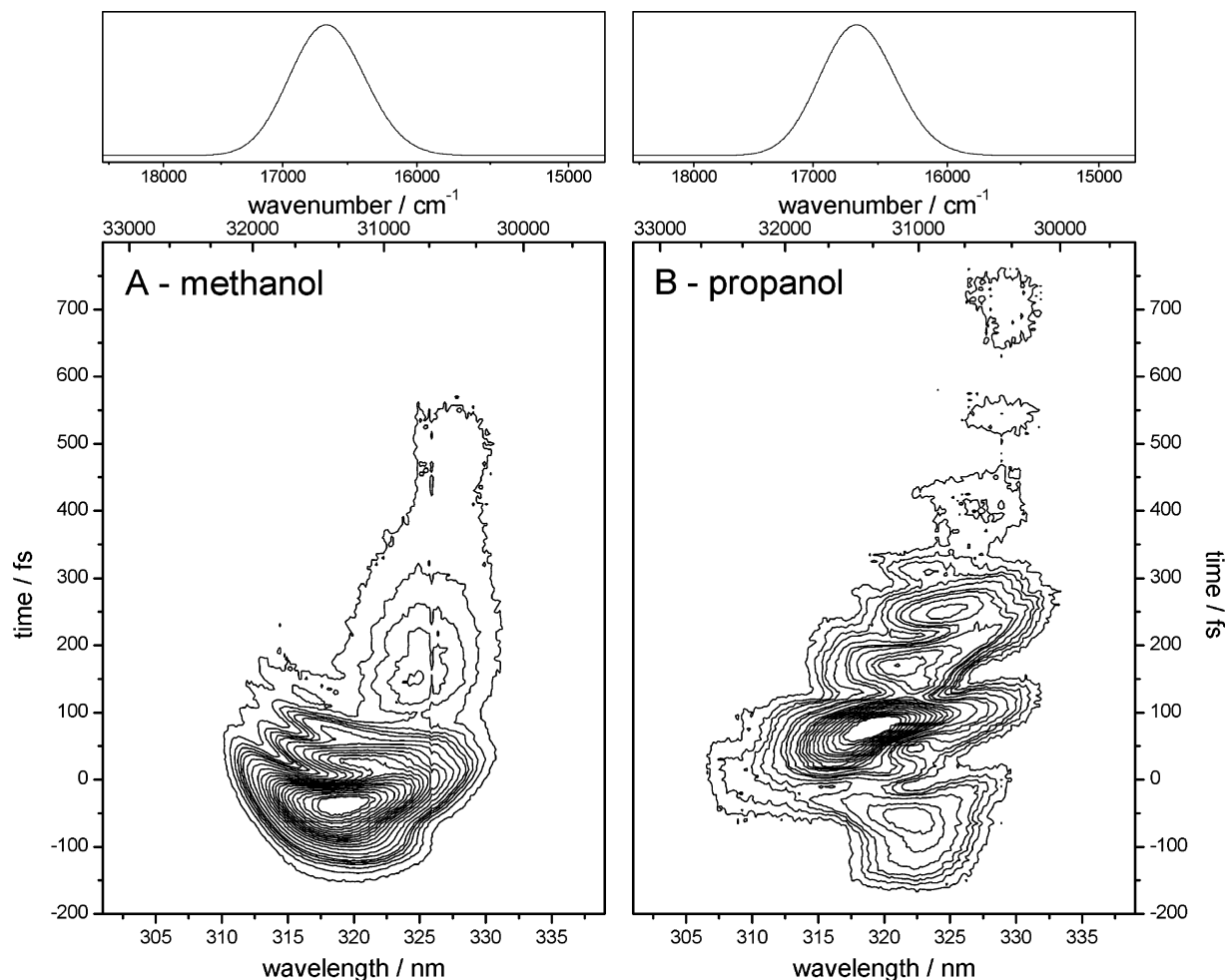


Figure 3. xFROG traces of the optimized pulses are shown. The traces were recorded by mixing the 600 nm optimized pump with the 680 nm transform-limited probe-pulses in a 30 μm thick BBO crystal and spectral dispersing the sum-frequency onto a diode array. To simplify the correlation with the absorption spectra shown in Figure 1, the spectrum of the 600 nm pump pulse is shown schematically in the top panels. The zero time of the xFROG traces corresponds to the position of the transform limited reference pump pulse.

slight details of the optimized pulse-shapes vary, the general features, which will be discussed in the following are reproduced. The most dominant effect of the pulse shaping was to impose negative chirp to the pulses as apparent in the resultant xFROG-traces. Panels A and B of Figure 3 depict the xFROG traces of the pulses minimizing isomer production in methanol and propanol, respectively. As can be seen, the dominant and most intense subpulse has its spectral maximum in the sum-frequency signal at around 318 nm (31450 cm^{-1}), while the trailing edges of the optimized pulses appear red-shifted and for long times exhibit a spectral maximum at around 328 nm (30490 cm^{-1}). Hence, over the full temporal duration of the optimized pulses, a significant Stokes shift ($\sim 1000\text{ cm}^{-1}$)—larger than the spectral fwhm of the transform limited pump-pulse ($\sim 670\text{ cm}^{-1}$)—is observed. This finding is in line with earlier experiments showing that excited-state population can be efficiently dumped back to the trans ground state by the pump pulse itself, when a suitable negative chirp is applied.^{22,23,33}

Distinct differences between the pump pulses optimized for reducing the number of photoproducted cis isomers in methanol and propanol are apparent. The pulse optimized to dump population of 1144C dissolved in methanol extends for about 400 fs. However, for 1144C dissolved in propanol the optimized pulse shown in Figure 3B appears more prolonged: considerable changes in pulse intensity are still visible after about 750 fs. Furthermore, the latter optimization in contrast to using methanol as solvent yields a pulse with distinct, well separated subpulses.

To gain more detailed insight into the pulse characteristics of the optimized pump-pulses, Figure 4A,B presents the xFROG spectra at different time cuts. In propanol, the spectrum of the optimized pulse is close to Gaussian over its entire temporal extent (Figure 4B). Following the maximum position of the spectrum directly reveals the dominant down-chirp. However, the spectra displayed in Figure 4A with methanol as solvent are slightly more complex and a multipeak structure is apparent (see discussion below). Nonetheless, in the time evolution of a particular maximum, e.g., the main maximum appearing initially at 31752 cm^{-1} or the shoulder, which is apparent at 31353 cm^{-1} at 0 fs, a characteristic down-chirp is observed.

The optimum chirp for dumping population back to the ground state is related to the relaxation dynamics on the ES-PES.^{22,23,32,33} As excited-state relaxation and solvation dynamics result in a dynamic Stokes shift of emission, an up-chirped pump-pulse is unsuited for optimized dumping. In this case excited-state relaxation drives the system quickly out of resonance with the successively blue-shifted laser spectrum. In the other extreme, if a very rapid down-chirp is applied, the increasingly red-shifted pump colors will be moving out of resonance with the slower change in stimulated emission frequency of the molecular system.

To the best of our knowledge, the data presented here directly reveal for the first time the excited-state wavepacket of a photoexcited cyanine motion in close proximity to the Franck-Condon point. A plot of the maximum of the xFROG spectra

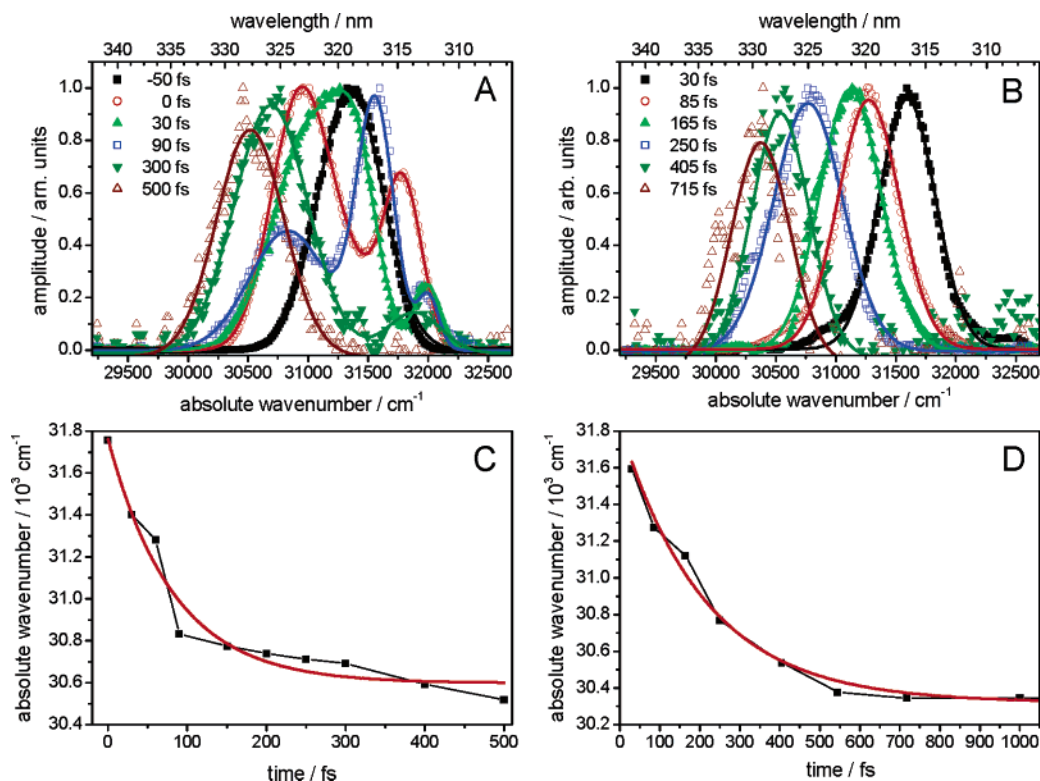


Figure 4. Normalized xFROG spectra of the optimized pulses (A, methanol; B, propanol) at different times. Times given in the insets refer to the time axes in Figure 3. Symbols represent experimental data; solid lines refer to (multi-)Gaussian fits. Maxima of xFROG spectra as a function of time obtained from the fitting procedure are shown in C (methanol) and D (propanol).

as a function of time (Figure 4C,D) mimics the time-dependent excited-state bond-twisting motion, which is accompanied by a shift in emission wavelength. To quantify the excited-state relaxation, a monoexponential fit to the data (Figure 4C,D) is performed, which is not meant to prove any model, as torsion motion is predicted to be nonexponential in close proximity to the trans geometry.^{30,31} However, such simple fitting approach is expected to yield considerable insight into the underlying system dynamics.^{5,28,29} The resultant fits underline the influence of the solvent viscosity on the photoreaction in 1144C: While the optimized pulse for dumping 1144C in methanol exhibits a down-chirp with a characteristic time of 81 ± 15 fs, the characteristic time of spectral shift in the propanol experiment is found to be slowed to 213 ± 28 fs. In qualitative agreement with experimental studies on 1144C^{25–29} and related systems,⁵ the solvent dependence of the excited-state relaxation is related to the increased solvent viscosity (0.55 cP, methanol, 2.20 cP, propanol) that decelerates photoinduced bond-twisting motion. In detail, theory predicts a fractional power dependence of the characteristic time scale of directed excited-state bond-twisting motion on the solvent viscosity, η , at small torsion angles.^{30,31} In contrast, the characteristic time of random Brownian torsion motion in the sink region, i.e., on a flat potential, scales linear with viscosity.^{30,31} The different solvent dependences of directed downhill and random torsion bond-twisting motion has been observed for the closely related molecule 1,1'-diethyl-2,2'-cyanine iodine and will be published in forthcoming work.³⁸ This work showed that random torsion motion at the bottom of the excited-state PES was proportional to the solvent viscosity, while the motion on higher lying parts of the S_1 -potential scaled as $\eta^{2/3}$.³⁸

The ratio of the characteristic times of down-chirp encoded in the optimized pulses as presented here yields $\tau_{\text{MeOH}}/\tau_{\text{PrOH}} = 0.38$. This value excellently correlates with the ratio of viscosi-

ties $(\eta_{\text{MeOH}}/\eta_{\text{PrOH}})^{2/3} = 0.39$. Thus, not only qualitative agreement with theoretical predictions^{30,31} but also quantitative agreement with a study on the closely related system 1122C is observed. The excellent correlation of the excited-state dynamics as revealed by the chirp characteristics of the optimized pulses with pump–probe data³⁸ further underlines the potential of the experimental approach pursued in this study.

From ground-state recovery and excited-state absorption decay times of 1144C published in literature,^{25–29} we estimated that the characteristic time for Brownian torsion motion in 1144C scales nearly linear with solvent viscosity in agreement with the findings for 1122C.³⁸ Thus, close to the Franck–Condon point, approximately the same curvature of the excited-state potential is to be expected for both 1122C and 1144C. This finding implies, that the much faster photoisomerization in 1144C compared to 1122C in a particular solvent is not related to a differently shaped PES. Our experimental results suggest that the solvent hinders the bulky-group torsion motion of the solute molecules fundamentally differently. Thus, it is necessary to use a local description of the solute–solvent interactions, when considering photoinduced excited-state isomerization.

It should be noted that the spectral evolution associated with torsion motion to the bottom of the excited-state potential is not entirely determined in the data presented here. The fluorescence up-conversion experiments presented in ref 28 show, that emission at 870 nm corresponds to a torsion-angle geometry that is only transiently populated. Thus, the spectral range spanned by the pump pulse in the experiments presented here by far does not cover the full range of emission wavelengths associated with the isomerization reaction of 1144C. Therefore, the long-time level of the xFROG maximum at about 30500 cm^{-1} is due to the spectral width of the pump pulses and not determined by the excited-state evolution. However, using the

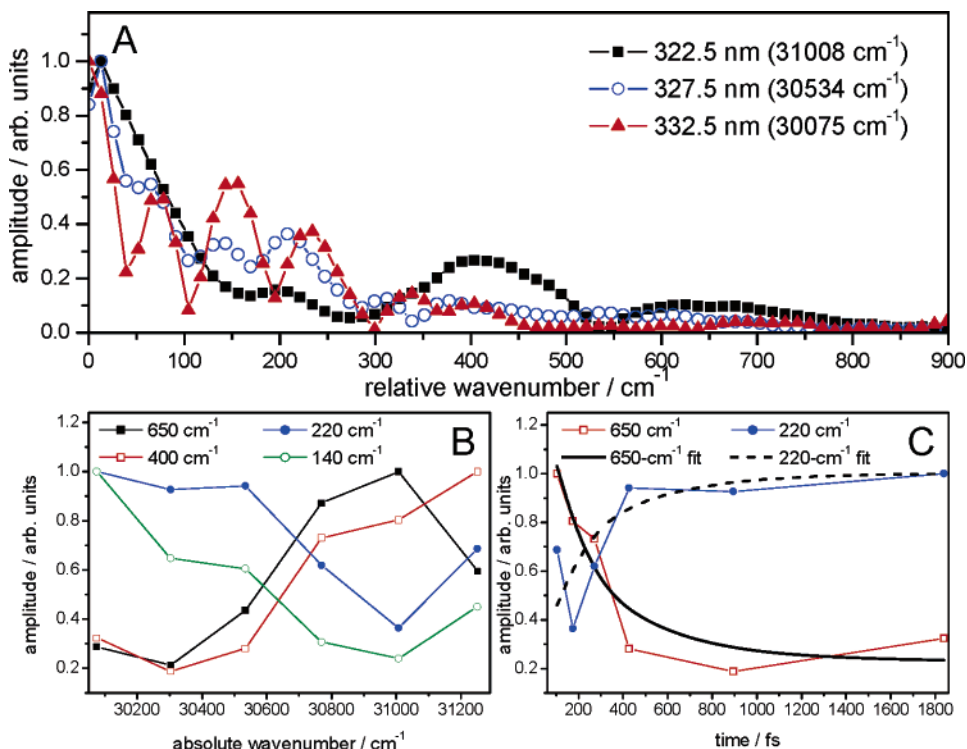


Figure 5. Fourier transforms of the time-dependent xFROG data measured at different wavelengths (A). The data refer to the pulse optimized for minimizing the isomerization yield of 1144C in propanol (see Figure 3B). Amplitudes of the modes appearing in the Fourier transform at 650, 400, 220, and 140 cm^{-1} as a function of xFROG-wavelength, i.e., their spectral position within the pump pulse (B). Time dependence of the amplitudes of the 400 and 220 cm^{-1} modes (C).

optimal control intrapulse pump-dump as a spectroscopic tool we gain access to the ultrafast bond-twisting motion near the Franck–Condon point, i.e., in a spectral region in which it is difficult to obtain ultrafast dynamics by means of conventional time-resolved spectroscopy. Furthermore, a pump–probe experiment reveals a global picture of light-induced processes but features that are non-critical for the observed dynamics might dominate the experimental data. For example, ground-state oscillations induced by a very short pump pulse might contribute significantly to differential absorption signals though they are completely unrelated to the excited-state dynamics.

Having discussed the solvent dependence of the rate of downchirp, i.e., the solvent dependence of the initial excited-state bond-twisting motion, we will now focus on the appearance of distinct subpulses in the propanol optimization, an observation that cannot be found in the case of methanol as solvent. As the pump pulse optimized to dump excited-state population of 1144C in propanol back to the ground state contains a train of well separated subpulses, it must be concluded that these substructures are related to vibrational motion of the dye itself.^{40,41} To specify the appearance of the temporal subpulse structure, Fourier transformations of the xFROG time-traces recorded at different wavelengths were performed (Figure 5). Figure 5A shows the amplitudes of the fast Fourier transforms (FFT) for different wavelengths across the pump-pulse spectrum. The spectra show distinct frequencies in the time structure of the optimized pulse train. Surprisingly, the spectral composition of the FFT changes, when scanning from the blue to the red edge of the excitation pulse. In the blue, the high-frequency modes at 650 and 400 cm^{-1} dominate, while at the red edge of the pulse spectrum, the lower-wavenumber modes contribute more to the temporal shape of the optimized pulse train (Figure 5B). The detailed reason for the spectrally dependent structure of the pulse train is unclear at the present stage of the investigation. However, the appearance of a particular mode

can be compared to the excited-state bond-twisting motion, which is reflected in the dynamic Stokes shift of the emission maximum (Figure 4C,D). An estimate of the time scale of the pulse-train structure changes can be obtained from plotting the relative amplitudes of the modes appearing in the FFT spectrum as a function of time (Figure 5C). The time scale in this figure is obtained from the dynamic Stokes shift of the emission maximum shown in Figure 4D. The decay and rise to the time evolution of the modes at 400 and 220 cm^{-1} can be fitted with a characteristic time-constant of 210 fs. Thus, the time evolution of the temporal composition of the pulse train correlates excellently with the overall downhill motion of the excited-state wavepacket.

A detailed inspection of the xFROG of the pulse optimized to dump excited-state population back to the trans ground state in propanol (Figure 3B) allows us to draw conclusions about the nature of the vibrational coherences reflected in the optimized excitation-pulse shapes. Though a dominant downchirp over the temporal duration of the optimized pump is observed, the individual subpulses appear to have either no chirp (trailing edge of the xFROG) or a slight negative chirp (leading side of the pulse). This finding indicates that the oscillation, which the optimized pulse structure is locked to, are not associated with torsion motion, i.e., they represent orthogonal modes to the bond-twisting motion being excited on the S_1 -PES. In detail, as these modes enhance the dumping of excited-state population, which is intrinsically coupled to the dynamics observed in stimulated emission, they must be associated with the excited-state dynamics.^{40,41} Ground-state vibrational wavepackets do not affect the emission properties of the excited state.^{40,41} Furthermore, the vibronic structure visible in the optimized pulse shape can be assigned to modes orthogonal to the bond-twisting reaction coordinate. Non-resonant Raman measurements on closely related systems have assigned a ground-state mode at 223 cm^{-1} to mutual twisting of the

quinoline moieties.⁴² However, a coherent wavepacket motion along the bond-twisting coordinate on the ES-PES would move the population through the spectral window accessible for dumping from larger energetic separation of the potential energy surfaces to smaller ones in one-half-period of the oscillation and vice versa during the second half-period. Therefore, a pulse train, in which two successive subpulses exhibit opposite chirp, is expected to most efficiently dump excited-state population if it is coherently oscillating along the FC-active bond-twisting reaction coordinate. This is obviously not found in the propanol experiment, and hence, it is concluded that the observed oscillations are associated with modes being orthogonal to the bond-twisting reaction coordinate, along which the S_1 – S_0 energetic separation does not vary considerably. This result qualitatively illustrates the validity of recent theoretical studies predicting the multidimensionality of the excited-state PES in cyanines to be of importance for a detailed understanding of the photoisomerization reaction.^{6–8}

Interestingly, vibrational coherences in nontorsion modes as discussed for the propanol experiment seem to be of minor importance for dumping when using methanol as solvent. We interpret this difference on the basis of the solvent viscosity of the excited-state relaxation. The initial fast bond-twisting motion, which is associated with stimulated emission wavelength within the spectral window covered by the pump pulse, is directly reflected in the spectral evolution of the optimized pump pulse. As for most efficient dumping, the spectral-temporal evolution of the pulse follows the stimulated emission dynamics of the investigated system, and the time scale of initial bond-twisting motion can be deduced from the time scale of spectral evolution of the optimized pulses. It is complete within approximately 160 fs ($2 \cdot \tau$) in methanol (Figure 4), while in propanol the ultrafast bond-twisting motion takes considerably longer ($2 \cdot \tau = 430$ fs).^{25,28–31,38} Hence, dumping can be considerably enhanced by locking the pump-pulse substructure to the internal clock provided by the vibrations of 1144C in propanol. On the other hand, the wavepacket motion of photoexcited 1144C in methanol is too fast in comparison to the vibration period of the non-torsion modes for the adaptive feedback loop to find a significant increase of the experimentally imposed fitness for the solution including vibrations.

However, the early part of the pulse optimized for dumping excited-state population in methanol (up to ~ 100 fs) shows indications of a pulse train, in which two successive subpulses exhibit opposite chirp (Figure 3). As discussed above, such chirp structure would be most efficient in dumping excited-state population in the presence of oscillations along the bond-twisting reaction coordinate. Interestingly, the observed oscillations show a characteristic period of roughly 50 fs. This finding is remarkable if we recall that bond-twisting motion is typically considered to occur in a rather shallow excited-state potential and calculations have yielded a time constant of 1.7 ps for the process in gas-phase.⁴³ Furthermore, in a viscous solvent environment torsion motion is drastically slowed.^{25–31,38} However, the fast oscillations might be rationalized, when considering that at each incident a given solute molecule due to interactions with the momentarily quasi-static surroundings experiences a local potential. These fleetingly existing potentials are much steeper than the global excited-state torsion potential schematically depicted in Figure 1. The isomerizing bond-twisting motion in concert with solvent fluctuations causes the solvent cage to somewhat alter its position, which in turn allows the molecule to relax into a slightly different temporal equilibrium structure. Nonetheless, momentarily the motion of a given

molecule along the reaction coordinate is restricted by the narrow local potential, which gives rise to the high-frequency oscillations reflected in the optimized pulse shown in Figure 3A. Along these lines of reasoning it has to be concluded that the torsion motion in propanol is much stronger damped compared to 1144C in methanol.²⁸ Therefore, the fast oscillations within the local potential are not required for efficient dumping. On the contrary, the overall slower population relaxation allows the feedback algorithm to address nontorsion vibrational modes to achieve an efficient reduction of the photoisomer production. Also, it can be speculated that the high solvent friction in propanol leads to considerably steeper local potentials than in methanol. In such situation the oscillations along the torsion coordinate might not be addressed during optimization due to the limited spectral bandwidth of the available pulses.

Conclusions

We report an optimal control experiment directly tracking the ultrafast excited-state bond-twisting motion in photoexcited 1,1'-diethyl-4,4'-cyanine in close proximity to the Franck–Condon point. The experimentally imposed objective, i.e., to reduce the number of cis isomers formed in the photoreaction, resulted in pump pulses with a prominent down-chirp structure in two alcohol solvents. This dominant feature can be rationalized in terms of an intrapulse pump-dump scheme. The evolution of the pump spectrum of the optimized pulses can be correlated with the reaction induced Stokes shift of stimulated-emission during the excited-state wavepacket dynamics. The pump pulse optimized for most efficient dumping of excited 1144C molecules in propanol exhibits pronounced subpulses. The temporal structure of this pulse-train reflects the intramolecular vibrations on the excited-state surface of 1144C in propanol. The subpulses do not exhibit alternating down- and up-chirp, as would be expected if the oscillation took place in the reaction coordinate, which predominantly changes the energetic separation between the excited- and ground-state PES. Therefore, it is concluded that the optimized pulse ensures most efficient dumping back to the trans ground state by accessing modes orthogonal to the bond-twisting coordinate, which are excited upon photoexcitation. Nonetheless, when using methanol to dissolve 1144C vibrational coherences, as observed for 1144C in propanol, seem to be less important for reducing the isomer formation in methanol. This observation is most likely related to the much faster downhill motion of the excited-state population in the less viscous solvent. Conclusively, the experimental approach pursued illuminates both diffusive and coherent ultrafast bond-twisting motion in close proximity to the Franck–Condon point that has been inaccessible by means of fluorescence up-conversion and transient absorption spectroscopy before. However, using adaptive feedback control as a spectroscopic tool the molecular properties and dynamics features are expressed, which are of essential importance for the interrogated process. Thereby, the data presented here selectively reveals those features, which are important to characterize the ultrafast bond-twisting motion.

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