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Communication: One-photon phase control of *cis-trans* isomerization in retinal

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We computationally demonstrate the one-photon phase control of retinal isomerization under conditions of low laser intensity. The calculations, utilizing the multiconfigurational time dependent Hartree method, include coupling between the two modes that are active in isomerization and the background molecular vibrational environment. Noting previously unsuccessful computations highlights the significance of this result. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4792834]

I. INTRODUCTION

The possibility of manipulating and controlling quantum systems is the goal of many modern laser-molecule studies.[1] An interesting type of control, one photon phase control, has been the subject of recent attention and discussion (see, e.g., Faraday Discussions 153[2]). In this case, control takes place by varying the relative *phase* of components of a weak pulse, while keeping the power spectrum of the light source fixed. A seminal proof[3] showed that one-photon phase control was not possible for closed molecular systems (i.e., systems not in contact with an environment) in which control is over products in the continuum. A subsequent experiment on control of retinal isomerization in bacteriorhodopsin[4] motivated controversy[5–8] and the need for clarification of conditions under which such control was possible. This clarification, provided in Ref. 9, showed that control was *possible* for both closed systems and for open quantum systems under well defined conditions. Specifically, we showed the following for control of an observable $\hat{O}$ in a system defined by Hamiltonian $\hat{H}_{\rm M}$:

(a) If the system is closed (i.e., not coupled to an environment), then one-photon phase control is possible if $[\hat{H}_{\rm M}, \hat{O}] \neq 0$. For example, control over isomerization in such a molecule is possible since the probability of observing an isomer (e.g., *cis* or *trans*) is an observable that does not commute with $\hat{H}_{\rm M}$. The situation is similar for control over product formation in radiationless transitions, such as intersystem crossing and internal conversion.[10] However, if $[\hat{H}_{\rm M}, \hat{O}] = 0$, then one-photon phase control is not possible in a closed system.

(b) If the system is open (i.e., coupled to an environment) then, as above, control is possible if $[\hat{H}_{\rm M}, \hat{O}] \neq 0$. However, even in the case where $[\hat{H}_{\rm M}, \hat{O}] = 0$ control may still be possible, in which case it is *environmentally assisted*.

Reference 9 derived these general rules and Ref. 11 provided insight into the way in which environmental assistance operates, and the conditions under which such control can be appreciable. For example, Ref. 11 demonstrated the significant role of non-Markovian dynamics and strong system-bath coupling in enhancing the extent of one-photon phase control and outlined formal conditions under which such control is manifested. However, although some simple one-dimensional model examples of one-photon phase control after excitation have been shown with a bath consisting of two level systems,[12] efforts to computationally demonstrate phase control in retinal have previously been unsuccessful. Here we overcome this challenge and computationally demonstrate one-photon phase control in a model retinal system.

The molecule 11-*cis*-retinal is the chromophore of rhodopsin and is covalently bound to the protein via a protonated Schiff base.[13–15] The absorption of light causes the photoisomerization of the chromophore to all-*trans*-retinal, inducing the protein activation and triggering a cascade of changes in the tertiary protein structure, ending up in an electrical impulse to the brain.[13] The photoisomerization process is known to occur coherently within 200 fs (for recent results see Ref. 16), an ultrafast process compared to the time-scale of the protein activation. This coherent motion may well continue after the molecule decays onto the ground electronic surface.[17–19] Related coherences were observed by Prokhorenko *et al.*[4] in bacteriorhodopsin, a protein containing retinal, a chromophore found in both bacterial and archaeal proton pumps and in the visual pigment rhodopsin. Specifically, they showed that weak tailored laser light pulses could be used to manipulate the efficiency of the isomerization. Measuring the photoproduct 20 ps after laser excitation showed a maximum yield control of ±20% when both laser amplitude and phase were varied. Interestingly, they also observed a 4% yield difference when changing the laser phase with fixed amplitude, i.e., one-photon phase control. As noted above, the experimental observation of phase control caused considerable debate. Here we computationally demonstrate phase control in a fully quantum mechanical multiconfigurational time dependent Hartree method (MCTDH) computation using a realistic retinal model.

II. PHASE CONTROL

A. Computational details

To describe the isomerization, we adopt the Hamiltonian of Stock and Hahn consisting of two electronic states and two modes[20,21] coupled to the 24-mode molecular vibrational backbone. The two mode model reproduces qualitatively well the first picosecond of the photoisomerization including the initial 200 fs dynamics, the 500 fs beating, and the high quantum yield. It consists of a torsional angle φ defining the *cis-trans* isomerization coordinate and a vibrational mode q, which are coupled to the ground and excited electronic states. In terms of the diabatic electronic states $|g\rangle$ and $|e\rangle$ this Hamiltonian in dimensionless coordinates is

$$\hat{H}_M(\varphi, q) = \sum_{n,m=g,e} |n\rangle h_{nm}(\varphi, q)\langle m|, \tag{1}$$

with $\hat{h}_{nm}(\varphi, q) = \hat{T}\delta_{nm} + \hat{V}_{nm}$, and

$$T = \frac{1}{2I}\frac{\partial^2}{\partial\varphi^2} + \frac{\omega}{2}\frac{\partial^2}{\partial q^2}, \tag{2a}$$

$$V_{gg} = \tfrac{1}{2}W_0(1-\cos\varphi) + \kappa q, \tag{2b}$$

$$V_{ee} = E_1 - \tfrac{1}{2}W_1(1-\cos\varphi), \tag{2c}$$

$$V_{ge} = V_{eg} = \lambda q, \tag{2d}$$

where I is the moment of inertia for the torsional degree of freedom, and ω the frequency of the normal mode, κ and λ are constants coupling the normal mode coordinate q to the electronic states. The electronic states $|g\rangle$ and $|e\rangle$ are coupled linearly in the q coordinate. The potential energy for the ground and excited electronic states as function of the torsional degree of freedom φ is shown in Fig. 1. Stock and Hahn then augmented this two-dimensional model with coupling to the 24 vibrational modes of retinal, known to contribute to the resonance Raman spectrum of rhodopsin. Within the harmonic approximation, the Hamiltonian of the additional modes is

$$H_B = \sum_{n=g,e} |n\rangle\langle n| \sum_{j=2}^{24} \left[\tfrac{1}{2}\omega_j\left(p_j^2 + x_j^2\right) + \delta_{n,e}c_j x_j\right]. \tag{3}$$

Since our interest below is in the population of the *cis* or *trans* configuration, the 25 other modes, bend plus vibration, are essentially the environment experienced by the system, which is itself comprised of the angle φ.

The total Hamiltonian is then given by $H = H_M + H_B$. The frequencies ω_j and excite-state gradients c_j are those given in Refs. 20 and 21. Since a computation with 26 nuclear degrees of freedom (DOF) on two electronic states is computationally challenging, we employ the MCTDH approach,[22] where, for a system with f DOFs $(q_1, q_2, \ldots, q_f)$, the wavefunction is assumed to be of the form:

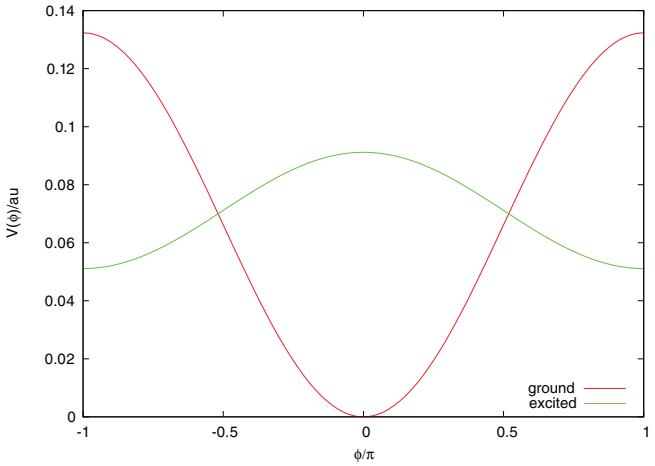

FIG. 1. Potential energy (in atomic units) as a function of the torsional degree of freedom φ.

$$\begin{aligned}\Psi(q_1, \ldots, q_f, t) &= \Psi(Q_1, \ldots, Q_p, t)\\ &= \sum_{j_1=1}^{n_1} \cdots \sum_{j_p=1}^{n_p} A_{j_1\ldots j_p}\varphi_{j_1}^{(1)}(Q_1, t)\ldots\varphi_{j_p}^{(p)}(Q_p, t)\\ &= \sum_J A_J \Phi_J,\end{aligned} \tag{4}$$

the $Q_\kappa = (q_a, q_b, \ldots)$ are composite coordinates, the $\varphi^{(\kappa)}(Q, t)$ are orthonormal time-dependent basis functions known as single-particle functions (SPFs). The J is a composite index used to simplify the notation, and the Φ_J are Hartree products of the SPFs. For an electronic DOF we only need to add an additional SPF into each Hartree product Φ_J. Using this ansatz in the time-dependent Schrödinger equation gives a set of equations for the coefficients A_J, and for the set of SPFs.[22]

The retinal is photoexcited using a linearly chirp pulse, where only the electronic degree of freedom interacts with the pulse:

$$\hat{H}_{\mathrm{SL}}(t) = -E(t)\hat{\mu}, \tag{5}$$

where $\hat{\mu} = \mu(|g\rangle\langle e| + |e\rangle\langle g|)$ is the transition dipole moment operator, and the laser is described classically as

$$\begin{aligned}E(t) = \epsilon_0 \exp\left[-4\ln(2)\left(\frac{t-t_0}{\tau}\right)^2\right]\\ \times \cos[\omega_{\mathrm{L}}(t-t_0) + d_{\mathrm{L}}(t-t_0)^2].\end{aligned} \tag{6}$$

Here t_0 and τ are the center and width of the Gaussian pulse envelope, ϵ_0 and ω_{L} are the laser field strength and carrier frequency, and d_{L} is the chirp rate. This chirp describes the time dependent variation of the laser carrier frequency. A positive chirp results in an increase in frequency with time, whereas a negative chirp results in a decrease. In this case, by varying the *sign* of the chirp d_{L} one is able to assess the dependence of the isomerization on the laser phase for fixed laser power spectrum. This means of examining the phase dependence of the dynamics is similar to that of Ref. 12.

The total Hamiltonian including the laser pulse is then $\hat{H} = \hat{H}_M(\varphi, q) + H_B + \hat{H}_{\rm SL}(t)$. For this non-autonomous Hamiltonian, the MCTDH method considers the time as a variable,[22,23] resulting in a 27 mode calculation: 26 nuclear DOF, one electronic DOF (with ground and excited states), and time. The excitation of the retinal is done in the presence of the coupled normal modes at all times. The calculations below utilize a laser with pulse width $\tau = 200$ fs and field strengths ϵ_0 in the range 10^{-6} to 10^{-5} a.u., the carrier frequency is obtained from 500 nm wavelength light, and the linear chirp constant is $d_L = 1.0 \times 10^{-7}$ a.u.

The total Hamiltonian $\hat{H}$ and the potential energy operator are separable which makes it easier to apply the MCTDH method to propagate the total wave function [Eq. (4)]. The primitive bases used depend on the specific degree of freedom. For the angle φ we use a periodic FFT basis, for the 25 normal modes we use harmonic oscillator basis, the electronic degree is introduced via the 2×2 matrix defined by Eq. (2).

B. Computational results

Results for excitation of retinal that is initially in the ground state of the ground electronic state are shown in Figs. 2 and 3. Specifically, Fig. 2 shows the probability of finding the system on the upper electronic state in the *trans* configuration. The positive chirp pulse is clearly seen to populate the *trans* configuration faster than does the negative chirp pulse.

Significantly, the notable difference between the probability of finding the system in the upper *trans* configuration for the positive and negative chirp continues with time, the probability being higher for the positive chirp pulse for all times after the pulse is over ($t > 800$ fs). In addition, the difference of the *trans* populations between the positive and the negative chirped pulses is seen to increase with the field strength. Also seen are oscillations of ≈200 fs in the positively chirped pulse case. Such oscillations are similar to those reported experimentally[15,17–19] and are presumed associated with coherent features of *cis/trans* retinal photoisomerization.

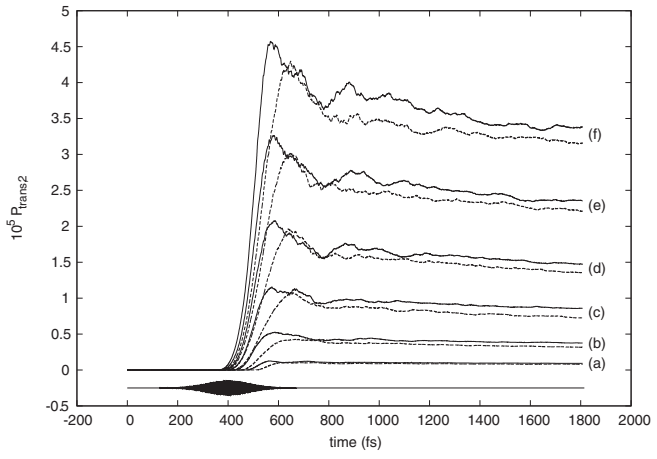

FIG. 2. Probability of finding the system on the upper electronic state in the *trans* configuration for different pulse strengths in atomic units (a.u.). The bottom-most curve represents the pulse in arbitrary units of force, (a) $\epsilon_0 = 1 \times 10^{-6}$ a.u.; (b) $\epsilon_0 = 2 \times 10^{-6}$ a.u.; (c) $\epsilon_0 = 3 \times 10^{-6}$ a.u.; (d) $\epsilon_0 = 4 \times 10^{-6}$ a.u.; (e) $\epsilon_0 = 5 \times 10^{-6}$ a.u. Solid line represents the positive chirp pulse and dash line represents the negative chirp pulse.

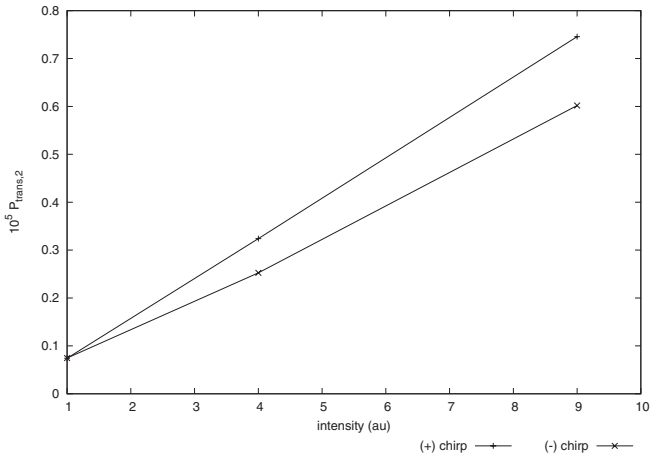

FIG. 3. Probability of finding the system in the *trans* configuration of the upper electronic state vs. pulse intensity (arbitrary units) after 800 fs.

Figure 3 shows the probability of finding the system in the *trans* configuration of the upper electronic state as a function of pulse intensity after the pulse is over. Designed to smooth out over the oscillations, these results were obtained by an exponential fit to the curves shown in Fig. 2 for times after 800 fs. A clear linear dependence on the intensity, expected in the one photon regime is observed, as is a clear difference in the probability of observing the *trans* configuration as a function of the sign of the chirp. Hence, phase control of retinal *cis-trans* isomerization is computationally demonstrated.

III. DISCUSSION

Several remarks are in order. First, note that MCTDH computations on this 26 degree of freedom are computationally intensive. As such, it was necessary for us to start with a single initial state, as opposed to the mixture expected in a typical non-state-selected experiment. Additional studies that are computationally prohibitive would be required to confirm phase control for an initial mixture. However, there is no reason to anticipate that phase control would be washed out by such an averaging. Second, it is interesting to note that the observation of an isomer constitutes the measurement of an observable $\hat{O}$ that does not commute with the molecular Hamiltonian. As such (see the Introduction) it would appear that the environment need not play a role in assisting phase control in this system. However, computational evidence indicates that this is not the case. For example, our previous studies using either a single-configuration method or Redfield theory did not yield phase control. This indicates, consistent with a more formal treatment,[11] that the character of the environment and of the system-environment coupling is crucial to the success of the phase control. For example, in our unpublished Redfield calculations, carried out beyond the secular approximation[24] $\omega_{ij} - \omega kl \leq \alpha_{\rm NS}$, with $\alpha_{\rm NS} = 0.02$ eV, the bath was treated as harmonic[25,26] and the system-bath coupling was described

with an Ohmic spectral density

$$J_a(\omega) = \frac{\pi}{2} \sum_\alpha g_{a,\alpha}^2 \delta(\omega - \omega_\alpha) = \eta_a \omega e^{-\omega/\omega_{a,c}}. \quad (7)$$

Here, the dimensionless parameter η_a describes the strength of the coupling between the ath degree of freedom and the bath, and the cutoff frequency $\omega_{a,c}$ gives the time scale distribution of the bath. We modeled different forms for the couplings between the system and the bath, including the one described above, Eq. (2). The laser pulse was also modeled as above. In all of our results we could not obtain the kind of significant amount of phase-control as is obtained here using the full MCTDH calculation. This may be due to the Markov approximation, implicit in the Redfield formalism. Specifically, this approximation does not necessarily eliminate one-photon phase control, but it may well weaken its effect.[11] Third, the bath here is given by the bend and vibrational components of the retinal molecule itself. Since this coupling is strong, we anticipate that this is the major contribution to decoherence and relaxation of the isomerization coordinate, with any additional bath degree of freedom associated with the protein environment being secondary. Fourth, the simple dynamics of *cis-trans* isomerization in a double well (i.e., in the absence of the vibrational environment) would show continuing time dependent oscillations between the *cis* and *trans* configuration as a function of time. By contrast, Fig. 2 shows that the population of *cis* or *trans* is relatively stable as a function of time, reflecting the role of the environment.

Our results clearly confirm the feasibility of phase control of isomerization in a complex polyatomic molecule, with support for the view that this effect benefits from system-environment interaction.

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