

## Phase structure of below-threshold harmonics in aligned molecules: A few-level model system

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We utilize few-level model systems to analyze the polarization and phase properties of below-threshold harmonics generated from aligned molecules. In a two-level system, we find that the phase of emitted harmonics undergoes a distinct change. For harmonics with photon energies below the transition energy between the dominant field-dressed states, the phase alternates by  $\pi$  between successive odd harmonic orders. In contrast, the phase remains constant for harmonics above the transition energy. Exploiting this behavior, we construct a four-level model composed of two uncoupled two-level systems aligned along orthogonal directions. We demonstrate that with selected transition frequencies lower-order harmonics follow the polarization of the linearly polarized driving field while higher-order harmonics exhibit a mirrored polarization. The model predicts that aligned systems with orthogonal transition dipoles may show analogous phase and polarization features in the below-threshold regime.

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**Introduction.** The mechanisms underlying below-threshold harmonics (BTH) in high-harmonic generation (HHG) from molecules driven by short, intense laser pulses differ fundamentally from the mechanisms responsible for the generation of higher-order above-threshold harmonics. In the gas phase, the latter typically involves a single active electron undergoing tunnel ionization to the continuum, followed by quasi-free propagation and recombination with the parent ion [1,2]. In contrast, below-threshold, nonperturbative harmonics may have substantial contributions produced by bound electrons that propagate under the force of the laser field along different electronic excited states. The time-dependent populations of the electronic states in the molecule and the related time-dependent dipole lead to the emission of harmonic radiation with photon energies below the ionization energy. Compared to above-threshold harmonic orders, the features of the BTH in molecules are much more target sensitive, as they are strongly influenced by the energy levels and the dipole transition matrix elements of the molecules. Its sensitivity makes BTH a valuable tool for high-harmonic spectroscopy [3–7] of molecules while their potential for VUV frequency comb generation [5,8,9] has further expanded their relevance. As a result, interest on BTH has grown significantly in recent years. The potential for spectroscopic insight comes to the price of complex analysis to unravel the multiple contributions [5].

While most studies apply semiclassical analyses to model BTH [5,10], which work well for very strong fields ( $I_0 \approx 10^{14}$  W/cm<sup>2</sup>), these models are inaccurate for smaller inten-

sities and obscure the role of discrete electronic transitions and their transition directions for the polarization properties of the emitted harmonics. On the other hand, a two-level model system (TLS) has been shown to reproduce features of the molecular harmonic response of  $H_2^+$  in the long-wavelength regime for more moderate fields [11]. As we are interested in the contribution of the bound-bound electronic transitions to the BTH, we turn to few-level model systems where specific transitions, dipole orientations, and resonances can be precisely controlled. Such simplified models offer a framework to investigate the mechanisms responsible for the complex polarizations of BTH from aligned molecules. Despite the simplicity of few-level models, they cannot be solved analytically beyond certain edge cases, like the rotating-wave approximation or approximate treatments using Floquet-Green formalisms [12]. However, even analytic approaches have revealed highly nontrivial harmonic phase behavior. For example, emitted plateau harmonics exhibit abrupt  $\pi$  phase jumps at specific Rabi frequencies [13]. These investigations were carried out in a parameter regime with extremely high field strengths where most population transfers between the adiabatic states occur at very distinct times. In such cases, analogies to the three-step model can be drawn [14].

To make the emission from a TLS similar to the contribution of a bound-bound transition to the BTH in a molecule, we will investigate the dependence of the harmonic phase in a TLS at more moderate field strengths and long wavelengths. Building on this approach, we present a model composed of two uncoupled TLS with orthogonal transition dipoles, to investigate how the phase properties of TLS manifest in the harmonic response of molecules with two distinct axes.

Consider the harmonic response of a TLS with the field-free Hamiltonian

$$\hat{H}_0 = \begin{pmatrix} -\omega_{10}/2 & 0 \\ 0 & \omega_{10}/2 \end{pmatrix}. \quad (1)$$

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We only allow for a single transition in the  $x$  direction, which simplifies the interaction part to

$$\hat{H}_1(t) = \begin{pmatrix} 0 & E_x(t)d \\ E_x(t)d & 0 \end{pmatrix}, \quad (2)$$

with the transition dipole moment  $d$  and an electric field of

$$E_x(t) = E_0 \text{env}(t) \cos(\omega_L t), \quad (3)$$

with the laser frequency  $\omega_L$ , the field strength  $E_0$ , and an envelope function  $\text{env}(t)$ . The total Hamiltonian reads  $\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t)$ . To investigate the electron dynamics, we solve the time-dependent Schrödinger equation (TDSE)

$$i \frac{d}{dt} \mathbf{C}(t) = (\hat{H}_0 + \hat{H}_1(t)) \mathbf{C}(t) \quad (4)$$

for the vector  $\mathbf{C}(t)$  describing the populations in the basis of the field-free orbitals, i.e.,  $|\Psi(t)\rangle = C_0(t)|\Psi_0(0)\rangle + C_1(t)|\Psi_1(0)\rangle$ . The TDSE is solved numerically using an explicit Runge-Kutta method of order 5(4) to obtain the time-dependent dipole  $D(t) = d(C_0^*(t)C_1(t) + C_1^*(t)C_0(t))$ . The harmonic spectrum is calculated via the Fourier transform of the dipole acceleration

$$H(\omega) = \|\mathcal{F}\{\ddot{D}(t) \times \text{hann}(t)\}\|^2, \quad (5)$$

with a hanning window  $\text{hann}(t)$ .

Our goal is to isolate and analyze the properties of harmonics that arise from a single bound-bound transition and to quantify its contribution to the overall molecular harmonic response. Therefore, we employ a two-level system with parameters chosen to represent a typical electronic excitation in an organic molecule. Throughout this work, atomic units are used. The transition frequency is set to  $\omega_{10} = 0.1$ , corresponding to an excitation energy on the order of a few electronvolts, and the transition dipole moment to  $d = -1.5$ . Both values are representative of the lowest singlet excitations in organic polyacenes [15]. The laser parameters, in particular the field strength and frequency, have to be chosen to circumvent plateau harmonics. This choice is necessary because, in physical systems, very strong fields and short wavelengths would lead to continuum transitions that dominate the harmonic response, which cannot be described within a TLS. We apply a Gaussian envelope of the form

$$\text{env}(t) = e^{-\frac{1}{2\sigma^2}(t - \frac{t_{\text{end}}}{2})^2}, \quad (6)$$

where  $t_{\text{end}} = 120\pi/\omega_L$  and  $\sigma = t_{\text{end}}/16$ . The electric field is smoothly brought to zero at the edges using a Tukey window.

Figure 1 shows harmonic spectra for different field strengths  $E_0$  at a driving frequency  $\omega_L$  that is 7.5 times smaller than the transition energy  $\omega_{10}$  ( $\omega_L = \omega_{10}/7.5$ ). We observe odd harmonics from order 3 to 17 as well as nonharmonic spectral features in between. Furthermore, we investigated the phase of the individual harmonics, which is found to be independent of the field strength in our parameter regime. This is in contrast to observations from Gauthey *et al.* with much stronger fields, for which avoided crossings of Floquet states lead to phase jumps [13]. Our field strengths are too weak to significantly change the Floquet states such that the phase jumps are absent.

However, we find a dependence of the harmonic phase on the frequency of the driving field. In order to provide context

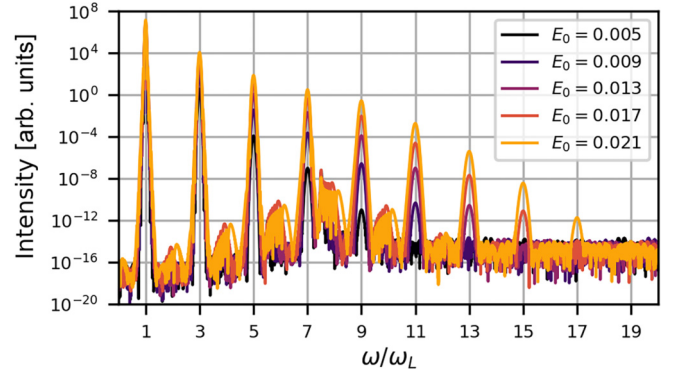


FIG. 1. High-harmonic spectrum of a TLS for different field strengths.

for the phase analysis, we calculate the harmonic yield for a constant field strength  $E_0 = 0.015$  and vary the laser frequency  $\omega_L$ . In Fig. 2, we show the spectral intensity plotted as a function of the ratio  $\omega_{10}/\omega_L$  and the harmonic order. We observe harmonics up to order 17. These harmonics appear as vertical lines. As  $\omega_{10}/\omega_L$  increases, higher-order harmonics are progressively enhanced, consistent with Ref. [16]. Whenever  $\omega_{10}/\omega_L$  is close to an odd integer (with an energy shift due to field dressing), the entire spectrum is enhanced. Such a global enhancement due to multiphoton resonances has been analyzed theoretically and experimentally in Refs. [16–20].

At  $\omega_{10}/\omega_L = 1$ , we see the tiny Mollow triplet of a TLS driven in resonance as side peaks around the fundamental that are split apart by the Rabi frequency  $\Omega = dE_0$ . For small deviations from  $\omega_{10}/\omega_L = 1$ , these satellite peaks move diagonally according to the change in the generalized Rabi frequency  $\sqrt{\Omega^2 + (\omega_L - \omega_{10})^2}$ , as predicted by the rotating-wave approximation. Outside strict resonance, additional nonharmonic spectral features appear between the odd harmonics due to superpositions of Floquet states. The primary resonance on the diagonal has additional satellite peaks spaced by integer multiples of  $2\omega_L$ , caused by the periodicity of the Floquet quasi-energy zones [21,22].

In Fig. 3, we analyze the phase of the harmonic orders as a function of  $\omega_{10}/\omega_L$ . Wherever the system emits odd

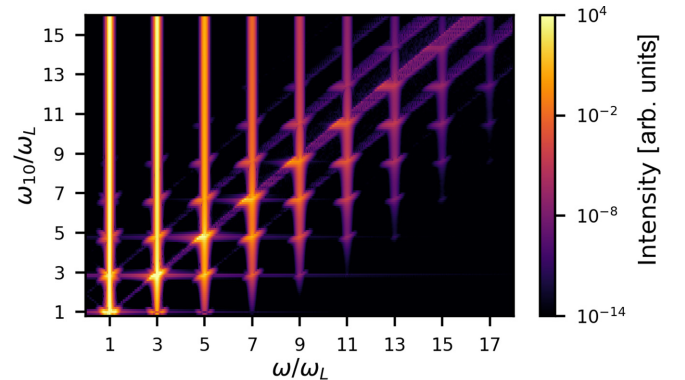


FIG. 2. Spectral intensity as a function of the ratio between transition frequency  $\omega_{10}$  and laser frequency  $\omega_L$  and harmonic order  $\omega/\omega_L$ . The plotted intensity is capped to the range  $[10^{-14}, 10^4]$ .

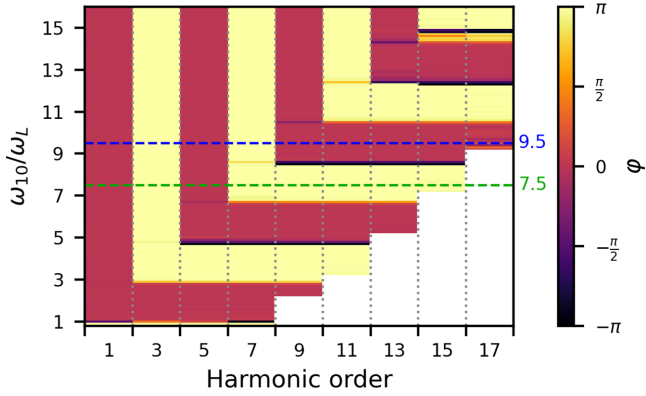


FIG. 3. The phase of the different harmonics plotted against the ratio between transition energy and laser frequency. The dashed lines indicate  $\omega_{10}/\omega_L = 7.5$  (green) and  $\omega_{10}/\omega_L = 9.5$  (blue), which are the relevant frequency ratios for the model in Figs. 4 and 5.

harmonics, we observe regions with either a phase of zero (red) or  $\pi$  (yellow) with respect to the phase of the driving field. Below the Floquet multiphoton resonance (harmonic order  $< \omega_{10}/\omega_L$ ), the phase of the different harmonic orders alternates between 0 and  $\pi$ , whereas above resonance, the phase remains constant. Whenever an odd number of photons matches the gap between the field-dressed states, a crossing appears in the Floquet band structure, altering the phase behavior. A similar observation was made by Gauthey *et al.* where a change in the Rabi frequency causes jumps of the harmonic phase precisely at locations of avoided crossings of Floquet states [13].

To analyze why the position of the resonance in the spectrum affects the phase of the emitted harmonics, we investigate the origin of the phase with an analytic expression. Within the adiabatic approximation, it is possible to derive a continued-fraction expression for the harmonics emitted by driving a TLS with a periodic laser field [23]. Further assuming that each successive harmonic order is substantially weaker than the previous one, the Fourier-transformed dipole  $\tilde{D}(\omega)$  of the  $n$ th harmonic can be expressed as a function of the preceding odd harmonic  $n - 2$  by

$$\tilde{D}(n\omega_L) = \frac{-e^{-2i\varphi_L} \frac{n-2}{n-1}}{\frac{2n^2}{n^2-1} + \frac{\omega_{10}^2 - n^2\omega_L^2}{E_0^2 d^2}} \tilde{D}[(n-2)\omega_L] \quad (7)$$

for the electric field  $E(t) = E_0 \cos(\omega_L t - \varphi_L)$  with the phase  $\varphi_L$ . For a derivation of Eq. (7), see Ref. [23] or the Supplemental Material [24] (see also Refs. [23,25] therein). We can extract the phase of the  $n$ th harmonic with  $\varphi_n = \arg(\tilde{D}(n\omega_L))$ . Note that the only terms in Eq. (7) that can be complex are  $\tilde{D}((n-2)\omega_L)$  and  $e^{-2i\varphi_L}$ . Therefore, within the limits of the approximations, for a real fundamental and  $\varphi_L = 0$ , i.e., a cosine pulse, all higher orders will be real as well. Consequently, the phase of the harmonics calculated with Eq. (7) can only assume  $\varphi_n \in \{0, \pi\}$ . If the prefactor in front of  $\tilde{D}((n-2)\omega_L)$  is negative, the harmonic phase will flip by  $\pi$  with each successive harmonic, and if the prefactor is positive, the phase will stay the same. The only term that, for  $\varphi_L = 0$ , can change the sign is the  $(\omega_{10}^2 - n^2\omega_L^2)/E_0^2 d^2$  term in the denominator. For our parameters, outside strict resonance, it will always be

larger than  $2n^2/(n^2 - 1)$ , as  $E_0$  is very small. This gives us the origin of the different behavior above and below the resonance: Below resonance  $\omega_{10}^2 - n^2\omega_L^2 > 0$ , retaining the minus sign in the prefactor, while above resonance,  $\omega_{10}^2 - n^2\omega_L^2$  is smaller than 0, which flips the sign in the prefactor. This behavior agrees with the numerical calculations shown in Fig. 3, except that if a harmonic is driven in resonance, the phase can assume values of  $\pm\pi/2$ , which does not occur in the analytic expression (7) because the adiabatic approximation breaks down for resonant driving. Note that the accumulation of the  $e^{-2i\varphi_L}$  phase for each successive odd harmonic is caused by the behavior of Fourier transformations with respect to time shifts, as a time shift by  $\Delta t = \varphi_L/\omega$  will give the  $n$ th harmonic the phase factor  $e^{-ni\varphi_L}$ . As a result, the phase of the harmonics relative to the phase of the driving field in Fig. 3 is dependent on the carrier-envelope phase (CEP). However, the CEP will not alter the characteristic switch in behavior above the resonance.

We now address how such phase behavior could manifest in physical systems. One possible signature is the polarization of harmonics emitted by two-dimensional molecules. Organic molecules can feature two dominant excited states with orthogonal transition dipole moments, such as acenes [26] and perylene bismides [27]. In such targets, if the harmonics' emission was governed primarily by two isolated bound-bound transitions, the response may resemble that of a two-dimensional model composed of two uncoupled TLS with different transition frequencies and orthogonal transition dipoles. In the following, we demonstrate how laser-frequency-dependent phase jumps directly translate into distinct polarization patterns of the emitted harmonics. We model the two-dimensional system with the field-free Hamiltonian

$$\hat{H}_0 = \begin{pmatrix} -\omega_{30y}/2 & 0 & 0 & 0 \\ 0 & -\omega_{21x}/2 & 0 & 0 \\ 0 & 0 & \omega_{21x}/2 & 0 \\ 0 & 0 & 0 & \omega_{30y}/2 \end{pmatrix}. \quad (8)$$

Both TLS have the same transition dipole strength but couple to different electric field components, leading to the interaction part

$$\hat{H}_1(t) = \begin{pmatrix} 0 & 0 & 0 & E_y(t)d \\ 0 & 0 & E_x(t)d & 0 \\ 0 & E_x(t)d & 0 & 0 \\ E_y(t)d & 0 & 0 & 0 \end{pmatrix} \quad (9)$$

of the Hamiltonian  $\hat{H} = \hat{H}_0 + \hat{H}_1(t)$ , with the electric field

$$\mathbf{E}(t) = \begin{pmatrix} E_x(t) \\ E_y(t) \end{pmatrix} = E_0 \text{env}(t) \cos(\omega_L t) \begin{pmatrix} \cos \alpha \\ \sin \alpha \end{pmatrix}, \quad (10)$$

where  $\alpha$  is the polarization angle relative to the  $x$  axis. We solve Eq. (4) numerically with the initial condition  $\mathbf{C}(0) = (1, 1, 0, 0)^\top$ . The two-dimensional dipole is obtained by calculating

$$\mathbf{D}(t) = d \begin{pmatrix} C_1^*(t)C_2(t) + C_2^*(t)C_1(t) \\ C_0^*(t)C_3(t) + C_3^*(t)C_0(t) \end{pmatrix} \quad (11)$$

and the total harmonic intensity with Eq. (5).

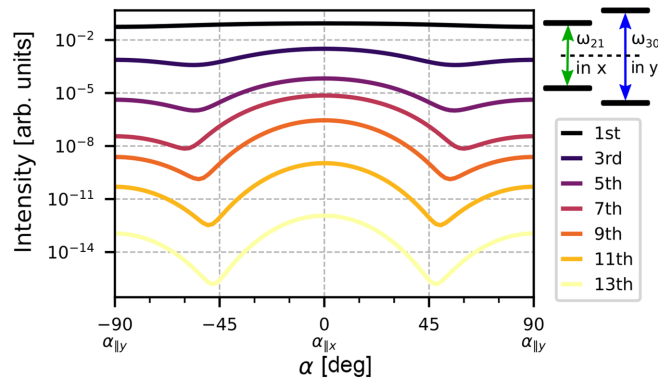


FIG. 4. Intensity of the harmonics in the four-level model system with two decoupled two-level systems as a function of the polarization angle of the driving field.

To ensure that the change in the phase behavior of the two orthogonal subsystems occurs for different harmonic orders, the transition frequencies are chosen as  $\omega_{21x} = 0.1$  and  $\omega_{30y} = 0.126$ . The frequency of the electric field is  $\omega_L = 0.1/7.5$ , placing the  $x$  resonance at  $\omega/\omega_L = 7.5$  and the  $y$  resonance at  $\omega/\omega_L = 9.5$  in the HHG spectrum. Furthermore, we use the same field strength  $E_0 = 0.015$ , envelope, and transition dipole moment  $d = -1.5$  as in the analysis for the single TLS.

The phase of the different harmonic orders for the two individual TLS is marked with the green ( $x$ -TLS) and blue ( $y$ -TLS) vertical dashed lines in Fig. 3. For harmonics below the transition energy of the green subsystem (harmonic order  $< \omega_{21}/\omega_L$ , up to order 7), the phases of the emitted harmonics from both subsystems are equal. As the blue subsystem has a transition energy that is  $2\omega_L$  larger, the above described change from the alternating phase (below resonance) to constant phase (above resonance) occurs for it at one odd harmonic order higher. Therefore, all harmonics above the seventh of the two subsystems will have a phase shift of  $\pi$  relative to each other.

Before analyzing the polarization properties of the harmonics, we briefly look at the intensities of the emitted harmonics, which are shown in Fig. 4 as a function of the polarization  $\alpha$  of the incoming laser pulse. The intensity shows maxima for an electric field polarized in  $x$  and  $y$  directions. In between, pronounced minima emerge near intermediate orientations. The excitation is most efficient when the driving field aligns with the transition dipole moment of a subsystem. Between these orientations, due to the nonlinear scaling of each subsystem's emission with the projection of the electric field on the transition direction, minima in intensity arise. The exact position of the minima also depend on the electronic structure parameters of the two TLS.

The polarization of the emitted harmonics is shown in Fig. 5 as a function of the polarization  $\alpha$ . Due to the discrete phase shift of 0 or  $\pi$  between the  $x$  and the  $y$  components, all harmonics are linearly polarized at an angle of  $\alpha_N$  to the  $x$  axis. The polarization angles of harmonics 1–7 show a monotonic increase as the polarization of the driving electric field is increased. However, due to the different scaling of the harmonics intensity of each subsystem, their polarization angles deviate from that of the incoming laser pulse.

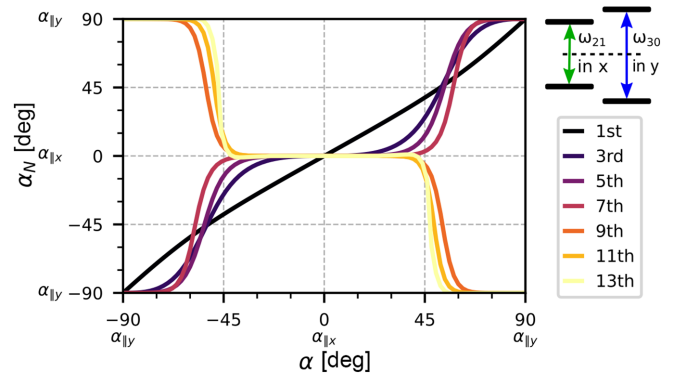


FIG. 5. Polarization of the harmonics in the four-level model system with two decoupled two-level systems as a function of the polarization of the driving field.

Starting from harmonic 9, we observe a different behavior. As  $\alpha$  is increased, the polarization of the harmonics rotates in the opposite direction than the polarization of the driving field. This is caused by the phase difference of  $\pi$  between the harmonics emitted by the two different TLS, effectively mirroring the polarization vector about the  $x$  axis, which leads to the “counterrotation” of the harmonic's polarization with respect to the polarization of the incoming laser field.

While this behavior looks similar to the two-center interference reported in HHG from aligned diatomic molecules [28], the microscopic origin is distinctly different. In  $H_2^+$ , interference between spatially separated emission centers produces similar amplitude minima and phase jumps for the high harmonic orders, which are energetically above the ionization limit. In our model, in contrast, the phase behavior arises from two uncoupled TLS with distinct transition frequencies,  $\omega_{21x}$  and  $\omega_{30y}$ , whose orthogonal dipoles lead to the observed signature in the amplitude and phase of the BTH.

We expect similar features for the bound-bound contributions to BTH in aligned molecules with orthogonal transition dipole moments of different electronic transitions. However, aligning suitable molecules in three dimensions along two principal axes is technically challenging. In addition, the presence of further excited states and continuum contributions to the generation of BTH in molecules might obscure the observed features.

An alternative way would be to measure the phase of the harmonics emitted by a single bound-bound transition directly using established methods such as the RABBIT (Reconstruction of Attosecond Beating by Interference of Two-photon Transitions) technique [29,30]. A suitable target should ideally possess a single dominant singlet transition that lies significantly below the ionization threshold. Furthermore, it might prove advantageous if the target either is spherically symmetric or can be aligned along a principal axis, as in the case of acenes.

From the theoretical side, the next step is to find traces of the discussed effect in realistic systems that include multiple electronic states, collective excitations, and the continuum. Such many-body simulations will guide the search for the predicted switch in the phase of the successive harmonics in real materials.

It would also be interesting to investigate whether interband contributions from crystals with relatively flat bands will show the same effect. This scenario could be experimentally accessible, as crystalline pentacene was recently shown to generate high-order harmonics with remarkable efficiency [31] and has intrinsic molecular alignment.

In future work, our improved understanding of anisotropic phase features will advance existing HHG-based orbital

tomography in aligned molecular targets. Focusing on the BTH may enable more detailed reconstructions sensitive to excited-state dynamics.

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*Data availability.* The data that support the findings of this article are openly available [32].

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