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To cite this article: Jibiao Li *et al* 2019 *J. Phys. B: At. Mol. Opt. Phys.* **52** 205101

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Coherent couplings between discrete sigma orbitals of carbon monoxide driven by external electric fields

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Received 4 April 2019, revised 26 May 2019

Accepted for publication 13 June 2019

Published 30 September 2019



CrossMark

Abstract

By applying external electric fields to an archetype diatomic molecule, CO, herein we have successfully observed coherent couplings established between two sigma orbitals of the CO molecule. By monitoring orbital evolution in real time, we have discovered that the two sigma orbitals pertain to coherent quantum oscillations in both the electric dipole and elemental charge. This finding essentially points to an important discovery that the electric fields selectively drive the sigma electrons onto new electronic orders of coherent orbital couplings. Such robust couplings among the sigma electrons can be well manipulated based on the discovery that the coupled oscillatory period is in proportion to the strength of the electric fields. Our investigations essentially have brought Bloch oscillations down to single molecular levels with new physical insights, thus opening up a new avenue to probe the very foundations of quantum mechanics with molecules, which may have insightful implications for attosecond correlation dynamics in molecules, and may have a profound impact on controlling electronic states by strong laser fields.

Keywords: carbon monoxide, sigma orbitals, electric field, coherent couplings

(Some figures may appear in colour only in the online journal)

External electric fields are truly one of the cradles for developing the quantum theory, particularly with regard to the Stark effect. In its original form, the Stark effect is known as spectral shifts and splitting in molecules, due to the presence of external electric fields [1–4], which serves as a starting point in understanding responses of molecules in external electric fields. Epstein's [5, 6] and Schwarzschild's concentration on linear and quadratic Stark effects based on Bohr–Sommerfeld quantum theory, Kramers's effort in modeling intensities of spectral transitions with the consideration of fine structure [7] and Pauli's first quantum mechanical modeling [8], as well as Schrödinger's

perturbation based quantum theory [9] readily come to mind on the essence of molecular science in electric fields. From a technical point of view, electric fields applied to molecules play a pivotal role in the state-of-the-art technology associated with molecules in strong laser fields [10–13] where electric fields can be well modulated in specific functions with respect to time. In this sense, Stark effect exerted by the laser fields turns out to be a crucial factor controlling the physics of molecule-laser interactions [14–16]. Although Stark effect has been known for centuries, how electric fields in Stark effect reshape electronic processes in molecules is a long-standing question to be resolved.

Molecular orbitals are at the heart of the Stark effect exerted by strong laser fields. Scientists have long envisaged

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being able to manipulate electrons in single molecular orbitals [17–20] so that they can get a glimpse into the question of what the effect of electric fields on molecular orbitals is. With diatomic molecules, scientists came to realize the dream of mapping out electrons in individual orbitals [21–24]. Although we have since witnessed the ability to probe the wave nature of electron correlation dynamics of individual orbitals with attosecond resolutions [25–34], probing electrons in single orbitals under electric fields remains a great challenge [35–38]. Moreover, a wide-held assumption is that individual molecular orbitals are independent in Stark shifting, and a static view has long been held for molecules in the presence of electric fields, hence any hidden connections between individual orbitals driven by external electric fields have scarcely been considered during the past century. Accordingly, we still lack fundamental understanding on symmetry mediated orbital cooperativity for molecules in electric fields, and the establishment of a link between the Stark effect and orbital interplays driven by electric fields is still lacking since the early days of quantum theory.

By applying electric fields to an archetype diatomic molecule, CO, in time-dependent density functional theory calculations, herein we have discovered strong couplings established between two σ orbitals of the CO molecule. By monitoring orbital evolution in real time, we have found that such couplings only exist amongst different sigma orbitals and represent a new class of orbital couplings beyond conventional electron correlations in molecules and solids. Unlike free CO molecules, we have discovered that the σ orbitals instigate coherent quantum oscillations in the electric dipole and elemental charge, providing novel evidence of controlled oscillatory couplings of sigma orbitals driven by external electric fields. Our findings actually highlight an important discovery: that electric fields selectively drive σ electrons onto a new electronic order of coherent couplings. We have actually provided a typical molecular analogue of Bloch oscillations, which exhibit the coherent coupling of quantum oscillations among sigma electrons, establishing the coherent marriage between the Stark effect and σ quantum oscillations.

In this work, all observables were calculated within the time-dependent density functional theory (TDDFT) framework [39]. The evolutions of the systems are described by a set of Kohn–Sham orbitals, which satisfy the time-dependent Kohn–Sham (TDKS) equations (atomic units are used throughout this paper unless otherwise stated):

$$i\frac{\partial}{\partial t}\psi_j(\mathbf{r}, t) = \left[-\frac{\nabla^2}{2} + V_{ks}(n; \mathbf{r}, t) \right] \psi_j(\mathbf{r}, t),$$

$$j = 1, 2, \dots, N. \quad (1)$$

N is the number of the occupied Kohn–Sham (KS) orbitals. The time-dependent electron density $n(\mathbf{r}, t)$ is given by $n(\mathbf{r}, t) = 2\sum_{j=1}^N |\psi_j(\mathbf{r}, t)|^2$. The TDKS potential $V_{ks}(n; \mathbf{r}, t)$

is defined as:

$$V_{ks}(n; \mathbf{r}, t) = V_{ion}(\mathbf{r}, t) + V_{Har}(n; \mathbf{r}, t) + V_{xc}(n; \mathbf{r}, t) + V_{ele}(\mathbf{r}, t). \quad (2)$$

In equation (2), the first term $V_{ion}(\mathbf{r}, t)$ represents electron–ion interactions described with norm-conserving Troullier–Martins pseudopotentials [40] in the Kleinman–Bylander form [41]. The second term $V_{Har}(n; \mathbf{r}, t) = \int [n(\mathbf{r}, t)/|\mathbf{r} - \mathbf{r}'|] d\mathbf{r}'$ is the time-dependent Hartree potential describing the interaction between electrons. The third term $V_{xc}(n; \mathbf{r}, t)$ is the exchange correlation potential, where we chose the generalized gradient approximation (GGA) proposed by Perdew, Burke and Ernzerhof [42, 43]. The last term $V_{ele}(\mathbf{r}, t) = \mathbf{r} \cdot \mathbf{E}(t)$ represents the interaction of the electrons with the external electric field.

The TDKS equation is solved and propagated using the software package OCTOPUS [44] in real-space grids with a time step of 0.045 a.u. (1 a.u. = 0.024 fs). The projection of the TDKS orbital $\psi_j(\mathbf{r}, t)$ onto the initial Kohn–Sham orbital $\psi_i(\mathbf{r}, 0)$ is obtained by:

$$C_{ij} = \langle \psi_i(\mathbf{r}, 0) | \psi_j(\mathbf{r}, t) \rangle. \quad (3)$$

For $\psi_j(\mathbf{r}, t)$, the time-dependent orbital dipole moment is calculated from:

$$\mathbf{d}_j(t) = \int \psi_j^*(\mathbf{r}, t) \mathbf{r} \psi_j(\mathbf{r}, t) d\mathbf{r}. \quad (4)$$

For each orbital, the electron charge is computed by $\rho_j = |\varphi_j|^2$, which is subsequently weighted by a mask function,

$$\mathbf{M}(\mathbf{r}) = \begin{cases} 1 & \text{if } |\mathbf{r} - \mathbf{r}_n| \leq 1 \\ 0 & \text{if } |\mathbf{r} - \mathbf{r}_n| > 1 \end{cases} \quad (5)$$

where \mathbf{r}_n is a vector for atomic positions, namely $\int \rho_i \mathbf{M}(\mathbf{r}) d\mathbf{r}$.

Applying external electric fields to the molecule, the adiabatic approximation is still valid when separating electrons from the nuclear. As a matter of fact, nuclear motions are on the picosecond timescales, and electron motions are on the attosecond-to-subfemtosecond timescales. So comparing the nuclear to the electrons in one periodic time period, the nuclear motions can be safely ignored. Taking a consideration of including nuclear motions into account would not change the overall results.

Coupled sigma quantum oscillations

By applying a static electric field, we observed contrasting projections for the respective σ (figures 1(a), (b)) and 1π symmetries (figure 1(c)); the σ electrons are subject to robust quantum oscillations, whereas the 1π electrons exhibit an oscillatory decay in real time. To our surprise, the projections involving the 4σ and 5σ orbitals show the exact same oscillatory period, indicating the hidden couplings between the two σ orbitals. The period we obtained for the 1π electrons is about 12.5 (a.u.) at the beginning, as evidenced by the 1π

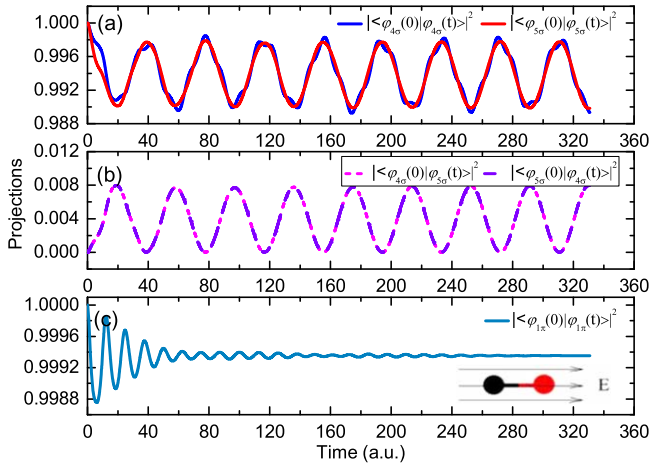


Figure 1. Quantum oscillations in sigma couplings. Time-dependent orbital projections of a CO molecule in a static electric field ($E = 0.0169$ (a.u.)). (a) $|\langle\varphi_{5\sigma}(0)|\varphi_{5\sigma}(t)\rangle|^2$ and $|\langle\varphi_{4\sigma}(0)|\varphi_{4\sigma}(t)\rangle|^2$, (b) $|\langle\varphi_{4\sigma}(0)|\varphi_{5\sigma}(t)\rangle|^2$ and $|\langle\varphi_{5\sigma}(0)|\varphi_{4\sigma}(t)\rangle|^2$ (c) $|\langle\varphi_{1\pi}(0)|\varphi_{1\pi}(t)\rangle|^2$. The free CO without electric fields shows two degenerate horizontal lines.

wavefunction projected onto its initial state. In contrast, the field gives rise to a different period $T = 39$ (a.u.) for the σ quantum oscillations. Mathematically, the σ and π waves are totally uncoupled, because the coherence function obviously points to zero. Physically, as $|\langle\sigma|\pi\rangle| = 0$ remains valid, the orthogonal nature between the σ and π orbitals would not change regardless of the external fields. A direct deduction from this observation is that couplings between σ electrons and π electrons are fundamentally prohibited.

Interestingly, we found symmetry-controlled coherence between two σ orbitals; coherent quantum oscillations can only be found within the occupied σ electron system that exhibits symmetry-mediated couplings. To examine the orbital couplings, we constructed orbital projections in four combinations of the two σ symmetries. The self-projected σ orbitals onto their initial states show robust coherence between the 4σ and 5σ orbitals (figure 1(a)), indicating the two sigma orbitals are highly coupled. Moreover, the two projections in crossing combinations show perfect coherence with exactly the same evolution (figure 1(b)), providing a solid support for sigma orbital couplings mediated by the quantum σ oscillations. The identical curves of the projections between the two σ orbitals give us a strong indication that there must be cooperative correlatives for the σ electron system in both real space and real time. The occupied σ orbitals are selectively activated to engage in the sigma orbital couplings with typical quantum oscillations occurring at attosecond timescales. Thereby we have essentially discovered one fundamental class of induced orbital couplings that operate solely in the σ electron system.

To explore the coherence on a practical level, we constructed symmetry resolved dipole moments (figure 2(a)). Besides the steady amplitude, the sine-like dipole evolution of the 5σ orbital shows robust period $T = 39$ (a.u.). A salient feature is that the initial dipole is not at the precise minimum. The restoration of the dipole moment sandwiches a small

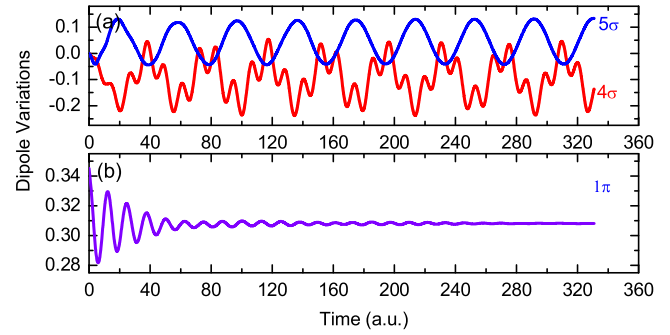


Figure 2. Quantum oscillations in dipole couplings. (a) Time-dependent electric dipole moments for the σ symmetries (4σ , 5σ) of a CO molecule with a static electric field ($E = 0.0169$ (a.u.)). The dipoles are shifted by their initial values, obtained as 0.9625 (a.u.) and -1.6715 (a.u.) respectively. (b) Time-dependent electric dipole moment of 1π orbital of a CO molecule with a static electric field ($E = 0.0169$ (a.u.)). Without applying an external electric field, we find that the variations of the time-dependent electric dipole moments for both the σ and π symmetries go to zero (10^{-6}).

dipole dip around each valley, suggesting the 5σ orbital is mostly of the *antielectric* nature, but can flip its dipole direction in the second order around each valley. Looking carefully upon the 4σ orbital, we found that its dipole evolution exhibits satellite peaks and valleys. The main peaks and valleys are repeated in the period T . Surprisingly, the curve is perfectly repeated by a doubled period ($2T$), strongly indicating that the two σ orbitals are in significant coherence in quantum oscillations. Most often, the electric field induces negative dipole moments in oscillation, suggesting the *paraelectric* nature of the 4σ orbital. However, the dipole evolution can be more positive in the vicinity of the dipole restoration, signifying rich physics of the 4σ electrons. In a word, we conclude that the *antielectric* nature of the 5σ orbital has to bring about the *paraelectric* nature of the 4σ orbital, or vice versa.

The 4σ and 5σ orbitals intrinsically have the respective parallel 0.9625 (a.u.) and antiparallel -1.6715 (a.u.) initial dipole moments with respect to the electric field. When applying an electric field orientated from the carbon to the oxygen, we observed that it always creates reversed dipole moments in the second order for the respective 4σ and 5σ orbitals, which have basically been divergent in directions. The 5σ is found to be *antielectric* because it creates an additional dipole moment pointing parallel to the electric field. Whereas the 4σ is *paraelectric* and generates an additional dipole pointing antiparallel to the electric field. Apparently, neither the *paraelectric* nor the *antielectric* response can exist alone, instead they are created in a pair by the electric field, signifying the deep couplings between the two σ orbitals.

In the first half-period, the diverging dipoles are accelerating in time evolution. The dipoles gain their maxima at the half period. In the second half-period, the two diverging dipole moments undergo deceleration and experience rich polarization during the dipole restorations around the valley (5σ) and peak (4σ). It is thought-provoking to wonder why

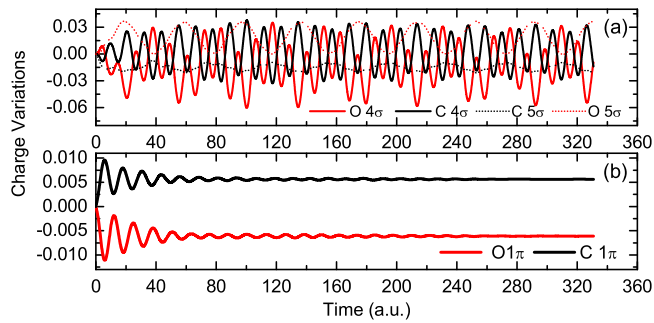


Figure 3. Quantum oscillations in charge couplings. (a) Atomic charges at sigma orbitals with a static electric field ($E = 0.0169$ (a.u.)), namely $O_{4\sigma}$, $C_{4\sigma}$, $O_{5\sigma}$, $C_{5\sigma}$, which are respectively shifted by their initial values, $O_{4\sigma(0)} = 0.5098$, $C_{4\sigma(0)} = 0.1372$, $O_{5\sigma(0)} = 0.0971$, $C_{5\sigma(0)} = 0.3271$. (b) Atomic charges at 1π orbital with a static electric field ($E = 0.0169$ (a.u.)), namely $O_{1\pi}$ and $C_{1\pi}$, which are shifted by their initial values, $O_{1\pi(0)} = 0.4526$, $C_{1\pi(0)} = 0.1297$. The scheme shows oscillatory couplings of the sigma electrons. Without applying an external electric field, the variations of the orbital-resolved charges for both the carbon and oxygen atoms go to zero (10^{-7}).

when gaining an additional dipole, antiparallel (*paraelectric*) to the field, by one σ orbital, has to result in a reversed dipole, parallel (*antieletric*) to the field for the other σ orbital. In other words, why would the rise (or drop) of the dipole moment in the 5σ orbital be accompanied by the drop (or rise) in the 4σ orbital? This observation provides solid evidence for the coherence in quantum oscillations exerted by the strong σ orbital couplings. The observation of the dipole moment of the 1π orbitals (figure 2(b)) reminds us that the electric field does not lead to oscillatory evolution in the 1π orbitals, again proving that the 1π electrons are not involved in the deep connections within the two σ orbitals.

Coherent sigma oscillations in real space

How are the σ electrons spatially coupled? In a particle view, a straightforward way to create a second-order dipole in an orbital is to have an electron hopping along the molecular axis. As the electric field is applied, electron hopping always simultaneously interacts with both the intrinsic orbital dipole moment and external electric field. As to the field applied along the carbon-to-oxygen direction, the intrinsic dipole moment of the 5σ orbital is actually antiparallel to the external electric field. The carbon-to-oxygen electron hopping is facilitated by the intrinsic 5σ dipole, but counteracted by the external field. The reversed hopping is, however, frustrated by the intrinsic dipole, but assisted by the external field. In contrast, everything is reversed on the 4σ orbital. For example, creating a positive dipole moment in the second order leads to electron hopping from the carbon to oxygen atoms, while a negative dipole moment in the second order reverses the hopping from the oxygen to carbon atoms. As the electric field is switched on, the quantum oscillations in the 5σ dipole are initiated by the oxygen-to-carbon hopping

followed by alternative carbon-to-oxygen and oxygen-to-carbon hopping.

The robust σ orbital couplings are further supported by orbital resolved charges on the carbon and oxygen atoms (figure 3). As far as the charges resolved by the 5σ orbital are concerned (figure 3(a)), we observed that the charge oscillations share the same period with the dipole oscillations. The field accumulates charges on the oxygen atom, while depleting charges on the carbon atom. This charge distribution is counteracting the external electric field, but facilitated by the intrinsic orbital dipole. However, the increase and decrease in the respective oxygen and carbon charges are clearly associated with electron hopping between the two atoms. In the first half-period, the divergence of the charges at the two atoms gives rise to increasing dipole moments, while the second half-period experiences a decreasing gap of charge. This observation strongly suggests that the 5σ electrons undergo dynamic polarization in perfect periodicity, where the oxygen maximum must correspond to the carbon minimum.

As for the 4σ orbital (figure 3(a)), we observed fine quantum oscillations that are in significant coherence with the 5σ orbital. In fact, the charge oscillations related to the 4σ orbital are approximately 7.5 times faster than the 5σ orbital regardless of the amplitude of the charge. For the 4σ orbital, we found perfect charge couplings on the two atoms as evidenced by the peak-to-valley correspondence, where charge accumulation on one atom leads to charge depletion on the other atom, strongly indicating the sigma orbital couplings with electron hopping along the molecular axis. We observed two types of peak-to-valley correspondence, which are respectively related to carbon-to-oxygen and oxygen-to-carbon electron hopping. The electron hopping is found to be alternating in real time, providing strong evidence for the electron oscillation within the 4σ orbital in real space. The oscillation between the carbon and oxygen atoms actually originates from correlated electron hopping within the single 4σ orbital. This is a unique type of electron correlation within an individual orbital, which is obviously driven by the external electric field.

In the wave view, the density of the oxygen atom has to be moderately increased while the density of the carbon atom has to be reasonably decreased. Such contrasting variations in oxygen density expansion and carbon density contraction would help to resemble the 4σ symmetry from the 5σ symmetry. There would be alternating density expansion and contraction on both the oxygen and carbon atoms. In other words, density expansion at one molecular end must bring about density contraction at the other end, and vice versa. The coupled σ electrons exhibit oscillatory expansion and contraction at the two molecular ends. This observation provides a direct link to the σ orbital couplings with the quantum oscillations, where the coupled σ electrons have to wobble back and forth between the oxygen and carbon atoms at attosecond timescales. In other words, the presence of the field induces oscillatory back-and-forth motion of the σ electrons in real space. The density expansion and contraction actually form the physical basis for the electron wavepackets

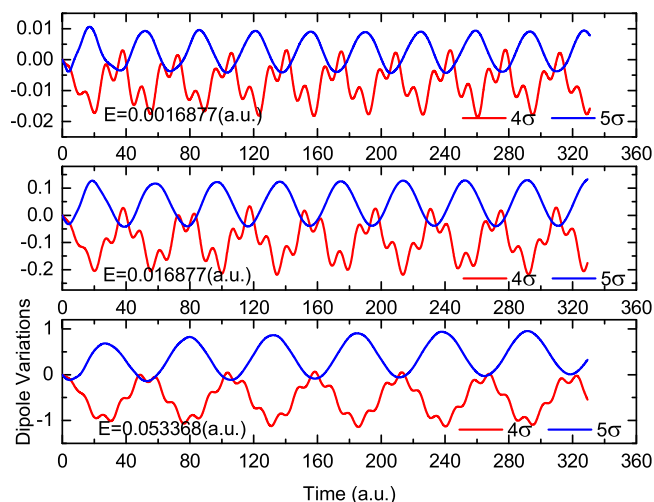


Figure 4. Controlling oscillatory sigma couplings by varying the electric field. We show electric dipole moments for the sigma electrons at three different electric fields. The dipole moments of the 4sigma and 5sigma orbitals are respectively shifted by their initial dipole moments. (a) $E = 0.00169$ (a.u.), (b) $E = 0.0169$ (a.u.), (c) $E = 0.0534$ (a.u.). The blue (red) curves are for the 5sigma (4sigma) electrons.

preparation. The wave nature of the density variations directly reflects the quantum mechanical picture of the σ orbital couplings.

In contrast to the 5σ orbital, the 4σ orbital is no longer neither purely paraelectric nor antielectric. Instead, it exhibits oscillatory switching between the paraelectric and antielectric nature. The 4σ orbital again shows paraelectric response to the field; the field depletes the charge on the oxygen atom, while accumulating the charge on the carbon atom. Examining the couplings between the two σ orbitals, we found that the σ orbital couplings have been established between the oscillatory polarizations in 5σ orbital and oscillatory hoppings in 4σ orbital. Again, the σ orbital couplings are established between two atomic-type correlations in respective 4σ and 5σ orbitals. We conclude that the oscillatory σ orbital couplings are created not only between the two σ orbitals but also within each of the two orbitals. Our results provide a fundamental picture for both the atomic-type correlation within individual orbitals and σ orbital couplings between two σ orbitals. Again, the evolutions of the charges on the 1π symmetry strongly suggest that the 1π symmetry is not involved in the σ orbital couplings because of the oscillatory decay in the presence of the external field (figure 3(b)).

Controlling the oscillatory sigma couplings

Thus far, we have established quantum mechanically where external electric fields drive the two σ orbitals onto the oscillatory couplings. As long as electric fields are present, the 4σ and 5σ electrons are always in deep and close couplings, which are intrinsically governed by the energy gap between the two σ orbitals and externally by the strength of the electric field. In other words, the robust couplings between

the two sigma orbitals can be reinforced and tuned by increasing the electric field (figure 4). There are fundamentally three types of coupled interactions. The first type concerns interactions of coupled σ electrons with respective σ dipoles. The second type has to do with interactions of the correlated σ electrons with the external electric field. The third type involves the field modulation of the respective σ dipoles. All three types of interactions contribute to the Stark shifts of the coupled σ orbitals.

The Stark shifts would cause variations in the gap between the two coupled σ orbitals, leading to changes in the period of the associated σ orbital couplings. However, the 4σ and 5σ levels normally counteract each other in responding to the external field. For instance, the Stark shifts of the two σ levels can be in opposite directions. The coupled σ electrons are not only subject to internal dipoles but also to the external field. As the electric field is set along the direction pointing from the carbon to the oxygen, the increase in the field strength would widen the gap due to Stark shifts. Surprisingly, we observed an oscillatory period $T = 34$ (a.u.) at $E = 0.00169$ (a.u.) and an increased period $T = 39$ (a.u.) for the enhanced electric field $E = 0.0169$ (a.u.) (figure 4). The amplitude of the σ quantum oscillation increases with the strength of the external electric field. We thus conclude that the period of the coherent σ couplings is proportional to the field strength and the σ orbital gap. This assertion is in sharp contrast to previous investigations on coherent oscillations between the two quantum states [45–48], where the period is inversely proportional to the energy gap [18, 27]. This discrepancy can be rationalized by the competing roles of carbon and oxygen $2p_x$ states in the sigma oscillations because the oxygen $2p_x$ state splits into the two parts that play dual roles in dipole oscillations. It is the oxygen $2p_x$ state connecting the 4σ and 5σ orbitals to respond to the Stark shift with a varied energy gap. As expected, results would be consistent with the coherent quantum states if the electric field is reversed to the O–C bond direction.

What is the difference between the dependence of sigma coupling on the electric field strength and coherent electron dynamics in molecular excitations? The central difference lies in how electrons respond to external approaches. When electric fields are applied to the molecule, Stark shifts occur in molecular orbitals. It is supercorrelation between different sigma orbitals fundamentally leading to the sigma coupling where the oscillation period is enhanced with increasing field strength. As for molecular excitations, however, coherent electron dynamics are highly dependent on the symmetry of a specific molecular orbital, and it does not have to be simultaneously controlled by two different orbitals.

To understand how the p electrons affect the sigma coupling, however, we should make some discussions on connections between p orbitals and sigma coupling. As can be observed from the MO diagram [49], only the oxygen $2p_x$ state contributes to the 4σ orbital, whereas the 5σ orbital finds contributions from both the oxygen and carbon $2p_x$ states. Applying the electric field to the CO molecule would definitely bring about oscillations of the 4σ electric dipole moment because the oxygen $2p_x$ state is simultaneously

experiencing two counteracting electric fields—the first of which is known as the external electric field and the second of which is the internal electric field built by the 4σ orbital. So the dipole has to oscillate in real time. As for the 5σ orbital, the oxygen and carbon $2p_x$ states overlap along the molecular axis. If the oxygen $2p_x$ state pertains to the 4σ oscillation, the connection between the oxygen and carbon $2p_x$ states must lead to 5σ oscillations in the electric dipole, which provides a fundamental basis for the orbital coupling between the two sigma orbitals. However, the periods for the respective 4σ and 5σ oscillations are not the same because there is a competition behind the connect between the oxygen and carbon $2p_x$ states. That is the reason why we observed small shoulders in the dipole oscillations. Furthermore, because carbon and oxygen $2p_y$ states are orthogonal to the molecular axis, there is clearly no driving force to move on the oscillation in the 1π orbital, which involves the carbon and oxygen $2p_y$ states, as the electric field is applied along the molecular axis. The 1π orbital is in sharp contrast to the 5σ orbital in which the oxygen and carbon $2p_x$ states show competing roles in dipole oscillations. That is the reason why the sigma rather than the pi oscillations go on and on.

We realize that the σ orbital couplings driven by the electric field are at the boundary of femtosecond and attosecond science, because the periods of the coupled σ oscillations are obtained as 34, 39, 54 (a.u.) for the increasing electric fields. In the attosecond regime, the Born–Oppenheimer approximation forms a cornerstone in understanding electronic processes. On the other hand, marching into the femtosecond scale is a double-sword for quantum oscillations. Vibrational couplings to the σ oscillations are inevitably strong in the femtosecond regime, in which another major concern is that the Born–Oppenheimer approximation might break down because of tardy electrons under high electric fields. In this sense, the external fields provide perfect choices to potentially realize the dream of capturing and manipulating induced orbital couplings in molecules. Spatially, the coupled 4σ orbital has to operate in the manner of decreased switching between the carbon and oxygen atoms with the increased electric field.

We believe that our attempt of using the carbon monoxide molecule as a probe to study the nature of orbital couplings would shed new light on experimental efforts towards manipulating emergent electronic orders in molecules and condensed matter. Our discoveries would not only deepen our understanding of orbital couplings in a more general context, but also impact our thinking about orbital control at attosecond timescales [50]. The hidden orders of electron couplings revealed in the current study strongly indicate that strong couplings induced by electric fields may be quite universal for molecules in strong laser fields. They probably hold the key to uncovering many mysteries in solids and molecules. Our findings may open up a new avenue to control coupled orbitals in quantum systems, which may have insightful implications for attosecond correlation dynamics, and ultimately may have a profound impact on orbital coupling puzzles exhibited in high-temperature superconductivity,

strong ferromagnetism and ferroelectricity, in the presence of external electrical fields.

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