

Asymmetry in orientation-resolved strong-field ionization of polar molecules

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We present calculations of orientation-dependent ionization yields from aligned H_2^+ and oriented polar HeH^{2+} and CO molecules by simulating the three-dimensional time-dependent Schrödinger equation. For the polar molecules, we observe asymmetries in orientation-resolved total ionization yields: The yields are not reflection symmetric across the orientation angle $\beta = 90^\circ$ with respect to the axis of the linear polarization of the laser field. A simple ionization model, applicable in the tunneling ionization regime, explains the asymmetry in ionization yields based on structural factors from weak-field asymptotic tunneling theory and asymmetries in the external field.

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I. INTRODUCTION

In strong-field ionization of atomic and molecular targets by intense laser pulses, the time-dependent Schrödinger equation (TDSE) is often solved within the single-active-electron (SAE) approximation to describe the ionization dynamics. Incorporating multielectron polarization (MEP) effects into the SAE framework enhances the predictions of strong-field observables such as total ionization yields (TIYs), above-threshold ionization spectra, photoelectron momentum distributions (PMDs), and high-harmonic generation (HHG) [1–3]. The inclusion of MEP has also stimulated considerable interest in the strong-field ionization of polar molecules (see, e.g., Refs. [3,4]).

It has long been argued whether or not polar molecules in strong fields can reveal clear signatures of their asymmetric molecular potential. Early experiments, however, typically employed probe pulses spanning several optical cycles with uncontrolled carrier-envelope phase (CEP) [5], making it impossible to control any directionality in the field with respect to the molecular orientation. Nevertheless, coincidence measurements made it possible to extract orientation-resolved features by detecting both fragment ions and tunneled electrons. For example, in the strong-field ionization of the polar HCl molecule by circularly polarized fields, asymmetry in the ionization yield was observed even with relatively long (50 fs) pulses, showing that the ionization probability along the molecular axis is asymmetric [6]. These asymmetries could only be uncovered through coincidence detection, which restores the molecular-frame information.

Later, TDSE simulations such as the study of water molecules in ultrashort intense laser fields [7] demonstrated that orientation-resolved ion yields depend sensitively on the CEP of the driving pulse, even for pulses lasting up to eight cycles. The reported asymmetry was attributed mainly to the permanent dipole moment of the molecule rather than to the orbital shape. It is worth noting that CEP-induced asymmetries have also been observed in PMDs for both polar and nonpolar systems, provided the pulses are sufficiently short (see, e.g., Refs. [8,9]). Effects of the permanent dipole in PMDs following strong-field ionization of polar molecules were pioneered in Refs. [10–12]. Here, however, we focus specifically on asymmetries in orientation-resolved ionization yields of polar molecules and explain the findings in terms of concepts from the tunneling ionization picture.

The aim of this work is to present a detailed investigation of the asymmetry in orientation-resolved ionization yields from polar molecules based on TDSE calculations and to rationalize the results using a tunneling-based model derived from weak-field asymptotic theory (WFAT) [13,14]. Among polar molecules, HeH^{2+} stands out as the simplest single-electron polar system, making it an ideal benchmark for probing the interplay between molecular asymmetry and strong-field dynamics. Early studies on HeH^{2+} [13,15,16] investigated orientation-dependent ionization rates using WFAT [13] and the molecular tunneling (MO-ADK) formula [16] and subcycle multiphoton ionization dynamics [15].

In this work, we investigate strong-field ionization of the single-electron molecules H_2^+ and HeH^{2+} . While the electron density of the 1σ ground state of H_2^+ is evenly distributed, the ground state of HeH^{2+} (1σ) is spatially localized primarily on the helium nucleus (taken along the positive z axis). We focus on how the molecular parameters of HeH^{2+} (structure factors and dipole moment) and the laser-field parameters (intensity, pulse duration, and CEP) influence the orientation-resolved ionization yields. To show the generality of our findings regarding the role of the molecular dipole, we also show results for the CO molecule.

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The TDSE is solved for oriented molecules exposed to linearly polarized laser pulses. Alignment- and orientation-resolved TIYs are obtained from the norm loss of the time-propagated wave function [17]. Our results show distinct asymmetries in the orientation-resolved ionization yields of HeH^{2+} and CO, which are absent in H_2^+ . In particular, for HeH^{2+} and CO, the angular yields are asymmetric with respect to the orientation angle $\beta = 90^\circ$ relative to the laser polarization. This asymmetry is strongly dependent on the pulse duration, and it gradually diminishes for longer pulses. We further show that a simple tunneling-based model grounded in WFAT [13,14] can qualitatively capture the main trends of the asymmetry.

The computational methods and theoretical framework are outlined in Sec. II, followed by results and discussion in Sec. IV, and concluding remarks in Sec. V. Atomic units are used throughout unless stated otherwise.

II. COMPUTATIONAL DETAILS

In our TDSE method, the time-dependent wave function $\psi(\mathbf{r}, t)$ is represented by a partial wave expansion in which the spherical harmonics $Y_{lm}(\Omega)$ are used to describe the angular degrees of freedom and a radial grid is used for the time-dependent reduced radial wave functions $f_{lm}(r, t)$, i.e.,

$$\psi(\mathbf{r}, t) = \sum_{lm} \frac{f_{lm}(r, t)}{r} Y_{lm}(\Omega). \quad (1)$$

The TDSE is solved in the presence of the external linearly polarized laser field. For the linear molecules, the potential is represented in a multipole expansion

$$V(\mathbf{r}) = \sum_l V_l(r) Y_{l0}(\Omega), \quad (2)$$

where the multipole potential $V_l(r)$ is obtained analytically for the considered one-electron systems, and the potential is generated numerically as described in Ref. [2] for the CO molecule. For the H_2^+ and HeH^{2+} one-electron systems, the multipole potential $V_l(r)$ is given by

$$V_l(r) = -\sqrt{\frac{4\pi}{2l+1}} \frac{r_{<}^l}{r_{>}^{l+1}} [Z_B + Z_A(-1)^l],$$

with $r_{<} = \min\{r, R/2\}$ and $r_{>} = \max\{r, R/2\}$, and Z_B (Z_A) the nuclear charge placed on the positive (negative) z axis.

The TDSE is propagated in the length gauge [18] with a combined split-operator [19] Crank-Nicolson method. The electric field $\mathbf{F}(t)$, linearly polarized along the laboratory-frame z axis, is defined as

$$\mathbf{F}(t) = F_0 f(t) \cos\left(\omega t + \varphi - \frac{\pi}{2}\right) \hat{z}, \quad (3)$$

$$\varphi = \frac{\pi}{2} \left(1 - \frac{\omega}{\alpha}\right) + \phi, \quad (4)$$

$$\alpha = \frac{2\pi}{\tau}, \quad (5)$$

where F_0 is the field amplitude, $f(t)$ the laser pulse envelope, and ω the frequency. The total phase φ includes a fixed term that aligns the carrier field with the center of the pulse envelope (for a laser pulse with duration τ) and an adjustable phase ϕ , which defines the CEP. The TDSE calculations were

TABLE I. Ground-state electronic energies E of HeH^{2+} and H_2^+ and dipole (μ_z , measured in Debye) along the internuclear axis of HeH^{2+} . For both molecules, the origin is in the geometric center halfway between the two nuclei, the distance between which is R . The dipole points from He (placed at $+z$ axis) to H.

System	R (a.u.)	E (a.u.)	μ_z (Debye)
HeH^{2+}	2	-2.491	-2.81
	3	-2.347	-4.47
	4	-2.295	-6.03
	5	-2.183	-7.57
H_2^+	3	-0.9119	-
	5	-0.7235	-

performed at laser frequencies of $\omega = 0.057$ a.u. corresponding to a wavelength of 800 nm. We use a trapezoidal envelope with a linear rise and fall of the pulse each taken to be equal to 20% of τ .

In the TDSE calculations for H_2^+ and HeH^{2+} , the radial grid contains 2048 points and extends to 240 a.u., and the size of the angular basis set is defined as $(l_{\max} + 1)^2$, where $l_{\max} = 40$. For CO, the radial grid has 1024 points and extends to 80 a.u., and the angular basis set has $l_{\max} = 60$. The calculations were performed at orientation angles in the range $\beta = 0^\circ - 180^\circ$ with a step of 15° . It is possible to calculate TIYs from numerical grid calculations by applying an absorbing potential $W(r)$ near the box boundary $r_{\max}$ of the form [20]

$$W(r) = \begin{cases} 1, & r \leq r_a, \\ 1 - \left[\cos\left(\frac{\pi}{2} \times \frac{r_{\max} - r}{r_{\max} - r_a}\right) \right]^{50}, & r > r_a, \end{cases}$$

where $r_a = r_{\max} - 50$ and the TIYs were produced from the norm loss [17]. After the end of the pulse, the TIYs were calculated after an extra field-free propagation time t_{extra} (where $t_{\text{extra}} = 9\tau$) to allow slow electrons to reach the absorbing boundary.

To show the precision of our approach for the molecular parameters, we give in Table I the electronic ground-state energies for HeH^{2+} and H_2^+ , as obtained by imaginary time propagation. These values are in reasonable agreement with quantum chemistry calculations. For HeH^{2+} , permanent molecular dipoles are shown as obtained from quantum chemistry calculations in GAMESS [21].

III. ASYMMETRY MEASURE AND MODEL

We refer to WFAT theory to quantify the asymmetry in the orientation- and internuclear-distance-resolved ionization probabilities. Note that for a given single-active-electron model potential, TDSE calculations include all effects related to the dynamics of the active electron in the external field, i.e., effects that can, in their appropriate limits, be explained in terms of, for example, tunneling concepts, multiphoton transitions, nonadiabatic effects, etc. The WFAT, on the other hand, is a strict tunneling theory; i.e., it is a time-independent theory that gives a prediction for a (time-independent) tunneling rate in a fixed static field. This means that any model based on WFAT or any other tunneling model will, by the

very nature of the problem, approximate the full TDSE when an oscillating laser field is considered. In the present work, the role of the WFAT theory and the proposed tunneling model is to rationalize the TDSE findings in terms of tunneling ionization in ionization time windows around the peaks in the half cycles: We are not trying to reproduce exactly the ionization yields using our simple model, but rather we are correlating asymmetries in orientation-resolved ionization yields with asymmetries in structure factors and asymmetries in laser pulse through a simple ionization model.

To quantify the asymmetry in the orientation- and internuclear-distance-resolved ionization probabilities, we consider the measure

$$A(\beta, R) = \frac{P(\beta, R) - P(180^\circ - \beta, R)}{P(\beta, R) + P(180^\circ - \beta, R)}, \quad (6)$$

where β is the angle of the molecule with respect to the polarization axis z . For a nonpolar molecule, symmetry implies that $P(\beta, R) = P(180^\circ - \beta, R)$, so the asymmetry in the TIYs is vanishing in this case, $A(\beta, R) = 0$. Note that there might be asymmetries in the photoelectron momentum distribution for nonpolar molecules for pulses containing a few cycles [9] but not in the TIYs. In the case of polar molecules, generally $P(\beta, R) \neq P(180^\circ - \beta, R)$, so for polar molecules we expect a nonvanishing $A(\beta, R)$. Below, we present TDSE results for this quality. To gain physical insights into these results, we now discuss a simple model for asymmetries in alignment- and orientation-resolved TIYs. The model relies on tunneling ionization concepts and, in particular, the weak-field asymptotic theory, where the ionization rate is expressed in terms of a product of a field factor and a structure factor [13,14].

Consider a molecule with internuclear distance R fixed at orientation angle β relative to the linear laser polarization defining the z axis of the laboratory fixed frame of reference. We consider a trapezoidal envelope laser pulse. The laser pulse has N_+ (N_-) number of peaks in the positive (negative) z direction. The ionization probability can be expressed as

$$P(\beta, R) \simeq N_+ P_+(\beta, R) + N_- P_-(\beta, R), \quad (7)$$

where $P_+(\beta, R)$ is the ionization probability when the field points in the positive z direction (from H to He; from C to O in the case of CO), and $P_-(\beta, R)$ is the ionization probability when the field points in the negative z direction (from He to H; from O to C in the case of CO). In the tunneling limit, the ionization process is exponentially sensitive to the field strength of the electric field, so the ionization probabilities of the molecule can be modeled by appropriate products of ionization rates and effective ionization time windows Δt centered around each half-cycle peak. For the linear molecules, we use the symmetries between P_+ and P_- at β and $180^\circ - \beta$ and obtain explicitly

$$P_+(\beta, R) = \Gamma(\beta, R) \Delta t, \quad (8)$$

$$P_-(\beta, R) = \Gamma(180^\circ - \beta, R) \Delta t, \quad (9)$$

$$P_+(180^\circ - \beta, R) = \Gamma(180^\circ - \beta, R) \Delta t, \quad (10)$$

$$P_-(180^\circ - \beta, R) = \Gamma(\beta, R) \Delta t, \quad (11)$$

with $\Gamma(\beta, R)$ the orientation- and internuclear-dependent tunneling ionization rate. In Eqs. (8)–(11), the factor Δt is presumed to vary during the rising and falling edges of the laser pulses. These variations should be disregarded because the ionization yield depends exponentially on the instantaneous field strength. As a result, the contribution to the total ionization yield from the weaker field peaks at the turn-on and turn-off stages of the pulse is negligibly small compared to that from the central region of the pulse, where the field reaches its maximum amplitude. Therefore, the variations in Δt associated with the edges of the laser envelope do not significantly influence the computed yields and can be safely neglected without loss of accuracy in the modeled ionization dynamics. Within the WFAT [13,14], which accounts for the presence of molecular dipoles, the rate to the leading order in the field strength F_0 is expressed as

$$\Gamma(\beta, R) = |G(\beta, R)|^2 W(F_0), \quad (12)$$

where $G(\beta, R)$ is the structure factor and $W(F_0)$ the field factor, which is independent of geometry. The field factor includes F_0 -dependent terms and most importantly the tunneling exponential factor $\exp[-2\kappa^3/(3F_0)]$, where κ relates to the ionization potential as $\kappa^2/2 = I_p$. The structure factor accounts for the molecular dipole along the z axis as well as the asymptotic form of the molecular orbital in the tunneling direction $g(\beta, R)$ through $G(\beta, R) = \exp(-\mu_z \kappa) g(\beta, R)$ [14]. For simple molecules, the determination of the molecular structure factors was described in Refs. [13,14]. The structure factor depends on the asymptotic form of the electron wave function in the tunneling direction. A compilation of structure factors was presented in Ref. [22], with a discussion on how the structure factors can be expanded in Legendre polynomials. Later, an all-electron approach was implemented (see Ref. [23] and references therein).

Inserting Eqs. (7) and (8)–(11) in Eq. (6), we obtain the following model for the asymmetry parameter:

$$A(\beta, R) = \chi(\beta, R) \xi(N_+, N_-), \quad (13)$$

where $\chi(\beta, R)$ relates directly to the molecular structure factors

$$\chi(\beta, R) = \frac{|G(\beta, R)|^2 - |G(180^\circ - \beta, R)|^2}{|G(\beta, R)|^2 + |G(180^\circ - \beta, R)|^2}, \quad (14)$$

and the field asymmetry is given by

$$\xi(N_+, N_-) = \frac{N_+ - N_-}{N_+ + N_-}. \quad (15)$$

For nonpolar molecules, the factors $|G(\beta, R)|^2$ and $|G(180^\circ - \beta, R)|^2$ are identical; $\chi(\beta, R) = 0$ and thereby $A(\beta, R) = 0$. So, for a nonpolar molecule, an asymmetric field cannot induce any asymmetry in the alignment-dependent ionization at β and $180^\circ - \beta$.

Turning to polar molecules, the factors $|G(\beta, R)|^2$ and $|G(180^\circ - \beta, R)|^2$ attain different numerical values (see Refs. [13,16]); therefore, $\chi(\beta, R) \neq 0$. In this case of a polar molecule, the asymmetry in the TIY depends on the field asymmetry parameter $\xi(N_+, N_-)$: the larger asymmetry in the field, the larger asymmetry in the TIY.

The asymmetry in ionization yields from Eq. (13) can be attributed to either the field asymmetries, represented by the

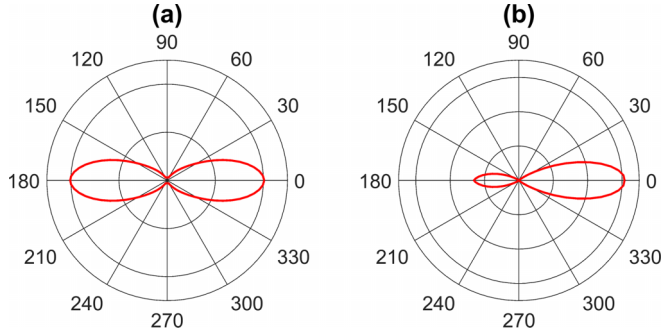


FIG. 1. Angular distribution of TIIYs from (a) H_2^+ ($R = 5$) and (b) HeH^{2+} ($R = 5$) as obtained from TDSE calculations at peak field values of 0.05 a.u. for H_2^+ and 0.25 a.u. for HeH^{2+} ; $N_{\text{cyc}} = 5$ and $\phi = 0$.

term $\xi(N_+, N_-)$, or the asymmetrical tunneling rates influenced by structural factors $|\mathcal{G}(\beta, R)|^2$ and $|\mathcal{G}(180^\circ - \beta, R)|^2$, expressed through $\chi(\beta, R)$. In Ref. [16], the tunneling ionization rate of HeH^{2+} is reported as a function of internuclear separation (R ranging from 2.0 to 4.0 a.u.) at a laser intensity of $5 \times 10^{15} \text{ W/cm}^2$. As R approaches infinity, it is anticipated that $\chi(\beta, R) \rightarrow 0$, indicating an atomic response with the orbital centered on one nucleus.

Note that the asymmetry factor presented in Eq. (13) can also be calculated based on ionization yields at CEP values of ϕ and $\phi + \pi$, which will be equivalent to ionization at orientation angles β and $180^\circ - \beta$. In TDSE calculations, when the laser polarization is not aligned with the molecular axis, the interaction couples different magnetic quantum numbers m_l , which increases the dimensionality and computational cost of the problem [18]. However, in the special case when the orientation angle is $\beta = 180^\circ$, the field along the molecular axis is effectively the negative of the field in the aligned ($\beta = 0^\circ$) case. This situation can be handled by applying a π shift to CEP while setting the orientation angle to $\beta = 0^\circ$, preserving axial symmetry. By exploiting this symmetry, m mixing is avoided, allowing the problem to be solved in a reduced-dimensional space and significantly lowering computational cost.

IV. RESULTS AND DISCUSSION

A. Strong-field ionization of the nonpolar H_2^+ molecule

In Fig. 1(a), we show orientation-resolved TIIYs from the H_2^+ ($R = 5$) molecule probed by a femtosecond laser pulse containing five optical cycles (at 800 nm wavelength), as obtained from TDSE calculations at peak field strength of $F_0 = 0.05$ and CEP $\phi = 0$. At the end of the laser pulses, the wave packet was field-free propagated until the ionization yields are converged (typically $t_{\text{extra}} = 9\tau$); the ionization yields were calculated from the reduction of the norm on the computational grid, following the procedure in Ref. [17]. The figure shows that the ionization yields are identical at the angles β and $180^\circ - \beta$, resulting in zero asymmetry: the asymmetry factor from Eq. (13) ($A(\beta, R) = 0$). This can be understood based on the fact that the structure factors $|\mathcal{G}(\beta, R)|^2$ and $|\mathcal{G}(180^\circ - \beta, R)|^2$ are identical for

H_2^+ [24], resulting in $\chi(\beta, R) = 0$ and, hence, no asymmetry, ($A(\beta, R) = 0$), independently of the asymmetry in the field.

B. Strong-field ionization of the polar HeH^{2+} molecule

Turning to HeH^{2+} ($R = 5$), the calculations were performed at peak field strength of $F_0 = 0.25$ and CEP value of $\phi = 0$. In Fig. 1(b), we see that the ionization yields are not identical at the angles β and $180^\circ - \beta$; that is, the ionization yields are not reflection symmetric across $\beta = 90^\circ$. In this section, we will explore the sensitivity of the asymmetry parameter to factors such as pulse length expressed in terms of number of cycles N_{cyc} , intensity, and internuclear separation, based on the tunneling-based ionization model discussed in Sec. III.

We conducted a series of TDSE calculations for HeH^{2+} at orientation angle $\beta = 0^\circ$ [where $A(\beta, R)$ reaches its maximum with respect to molecular orientation relative to the laser polarization axis] and pulse durations ranging from $N_{\text{cyc}} = 4$ to 15. In Fig. 2(a), we show plots of the ionization yields from HeH^{2+} against the number of cycles N_{cyc} , at CEP values of $\phi = 0$ (solid line) and $\phi = \pi$ (dashed line) at peak field strength of $F_0 = 0.25$ (our choice of CEP values corresponds to orientation angles of $\beta = 0^\circ$ and $\beta = 180^\circ$). The ionization yields show CEP dependency even in the long pulse limit: The ionization yields are not identical for CEP values of 0 and π at all pulse durations being considered. This is contrary to the common understanding of strong-field ionization based on experience from symmetric molecules; see results for H_2^+ in Fig. 1. The asymmetry parameter [$A(\beta, R)$] plotted on the right axis of Fig. 2(a) tends to decrease, although not monotonically, with increasing pulse duration.

Now we will use the ionization model (introduced in Sec. III) to understand the dependence of ionization yields and asymmetry parameter on pulse duration. To this end, we show in Fig. 2(b) the numbers of positive and negative peaks (denoted as N_+ and N_-) for laser pulses with trapezoidal envelopes and CEP values of 0 and π , plotted against the total pulse duration (N_{cyc}). In the asymmetry model, we only include field peaks corresponding to the maximum field strength within the laser pulse envelope. Consequently, the peaks that occur during the rising and falling edges of the pulse are omitted. This simplification is physically justified because the ionization yield depends exponentially on the instantaneous field strength. It should be noted that at CEP values of 0 and π , the laser pulses exhibit asymmetry, characterized by differing counts of N_+ and N_- . The field asymmetry $\xi(N_+, N_-)$ tends to decrease, although not monotonically, with increasing pulse duration, as illustrated in Fig. 2(b) (right axis).

Finally, we turn our attention to Fig. 2(c), which shows a plot of the asymmetry factor $A(\beta = 0, R = 5)$ against $\xi(N_+, N_-)$ for laser pulses containing $N_{\text{cyc}} = 4-15$ (each point on the plot corresponds to a specific pulse duration) with a field strength of 0.25 (triangles, solid regression line) and 0.2 (circles). Here, two conclusions can be drawn. First, the asymmetry $A(\beta = 0, R = 5)$ has a good linear correlation with $\xi(N_+, N_-)$ with two exceptions where the calculations show significant deviation from the line; these are highlighted in the figure by the dashed circles. These exceptions correspond to pulses with $N_{\text{cyc}} = 8$ and 13, where the trapezoidal pulses

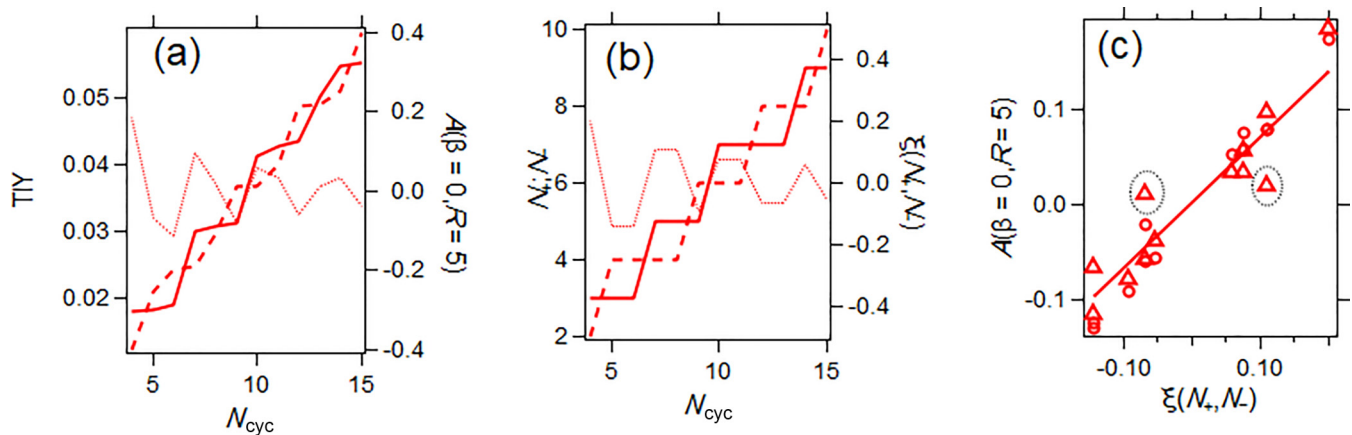


FIG. 2. (a) TIY from HeH^{2+} ($R = 5$) for laser pulses containing $N_{\text{cyc}} = 4-15$ with peak electric field of 0.25 a.u., trapezoidal envelope, and CEP of 0 (solid line) and π (dashed line). The asymmetry factor $A(\beta = 0, R = 5)$ (denoted by dotted line) is plotted on the right axis of panel (a). (b) Number of positive (solid line) and negative (dashed lines) peaks (N_+ , N_-) for laser pulses with trapezoidal envelope containing $N_{\text{cyc}} = 4-15$. The field asymmetry $\xi(N_+, N_-)$ (denoted by dotted line) is plotted on the right axis of panel (b). (c) Asymmetry factor $A(\beta = 0, R = 5)$ vs $\xi(N_+, N_-)$ for laser pulses containing $N_{\text{cyc}} = 4-15$ with field strength of 0.25 (triangles, solid regression line) and 0.20 (circles).

show peaks during the rise and fall of the pulse with field strength near the peak value. While these peaks affect the ionization yield and asymmetry, they are omitted from our model calculation of $\xi(N_+, N_-)$. Apart from these cases, we find a reasonably good line fit for the correlation between $A(\beta = 0, R = 5)$ and $\xi(N_+, N_-)$. Second, we note that the line fit is rather insensitive to laser intensity, as can be judged from the figure, where calculations at laser peak strengths of 0.25 and 0.2 show rather similar asymmetry values and follow almost the same line. The relative good agreement with the scaling predicted by the model shows that the ionization dynamics for both these field strengths are in the tunneling regime.

Now we address the effect of CEP on the observed asymmetry. The CEP affects the number of positive and negative peaks a laser pulse contains, and hence directly affects the field asymmetry parameter $\xi(N_+, N_-)$. Note that changing the CEP values from $(0; \pi)$ to $(-\pi/2, \pi/2)$ results in a reduction of the asymmetry parameter $A(\beta, R)$ as can be seen in Fig. 3. At the CEP values of $(-\pi/2, \pi/2)$, the laser pulses contain

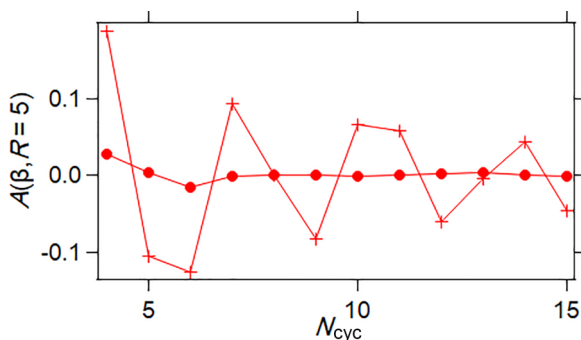


FIG. 3. Asymmetry vs pulse duration (N_{cyc}) in strong-field ionization of HeH^{2+} ($\beta = 0^\circ$, $R = 5$) for CEP values of $(0, \pi)$, denoted by "+" in the figure, and $(\pi/2, -\pi/2)$, denoted by filled circles in the figure, at a peak electric field value of 0.25 a.u.

the same number of positive and negative peaks; that is the field asymmetry parameter $\xi(N_+, N_-) = 0$.

Finally, we address the effect of internuclear separation on the asymmetry in the ionization yields of HeH^{2+} . To correlate the asymmetry with the changes in internuclear separation, we plot in Fig. 4(a) the asymmetry parameter $A(\beta, R)$, dipole moment (μ_z), and an orbital structural parameter against the internuclear separation (R). The structure parameter is represented here by the ratio $P_{l=1}/P_{l=2}$ from a partial wave decomposition of the highest occupied molecular orbital (HOMO), where $P_{lm} = \int_0^\infty |f_{lm}(r)|^2 dr$ with $m = 0$ for HOMO orbital of HeH^{2+} . We observe that while the asymmetry is decreasing with R , the dipole moment (μ_z) of the molecule increases. Meanwhile, going to longer internuclear separations results in lower $P_{l=1}/P_{l=2}$ in the partial wave decomposition of the HOMO orbital. In this sense, the evolution of the asymmetry with R is connected to the exact

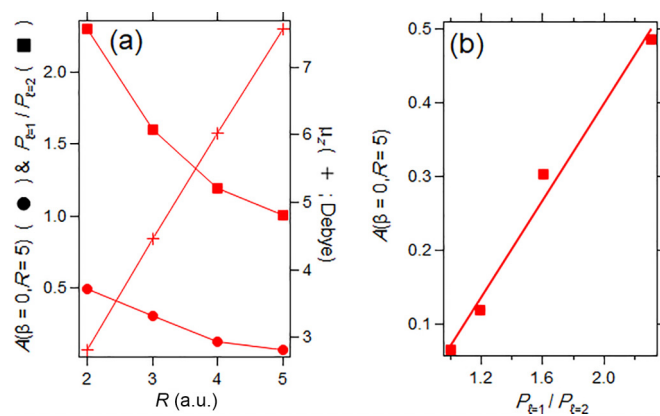


FIG. 4. (a) Asymmetry in ionization yields of HeH^{2+} $A(\beta = 0, R = 5)$ (filled circles), molecular dipole μ_z (+), and partial wave probability ratio $P_{l=1}/P_{l=2}$ (filled squares) plotted as a function of internuclear separation R for pulses with $N_{\text{cyc}} = 5$ with peak electric field of 0.25 a.u. and CEP = 0. (b) Correlation between asymmetry $A(\beta = 0, R = 5)$ and the ratio $(P_{l=1}/P_{l=2})$.

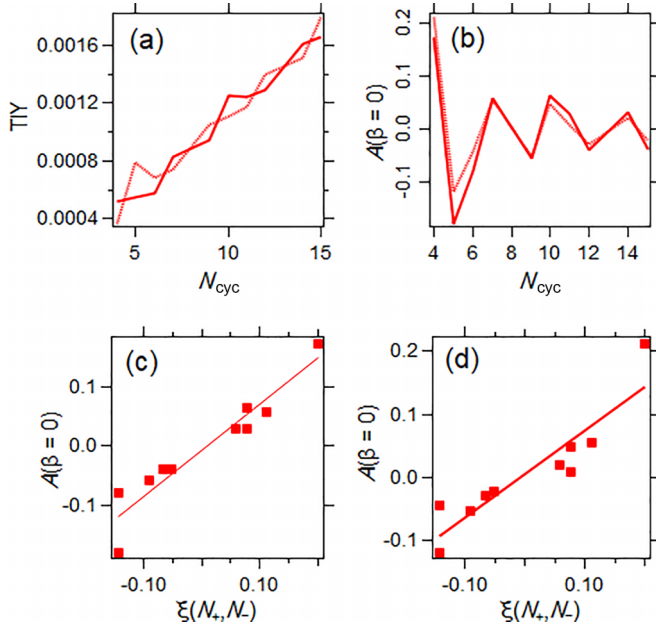


FIG. 5. (a) TIY from CO ($\beta = 0$) laser pulses containing $N_{\text{cyc}} = 4-15$ with peak electric field of 0.04 a.u., trapezoidal envelope, and CEP = 0 (solid line) and π (dotted line). (b) The asymmetry factor $A(\beta = 0)$ vs N_{cyc} for laser pulses with peak electric field of 0.04 a.u. (solid line) and 0.05 a.u. (dotted line). The asymmetry factor $A(\beta = 0)$ vs $\xi(N_+, N_-)$ for field strength of (c) 0.04 and (d) 0.05.

shape/structure factors of the HOMO orbital as illustrated in Fig. 4(b).

C. Strong-field ionization of the polar CO molecule

In this section, we show that the presence of asymmetry in orientation-resolved TIYs is common for the general case of polar molecules. However, two criteria are needed to have the asymmetry observed in strong-field simulations or experiments. First, the structure factors should be significantly different at β and $180^\circ - \beta$, resulting in $\chi(\beta) \neq 0$. Then, the CEP should be chosen such that the laser field is asymmetric as well, i.e., $\xi(N_+, N_-) \neq 0$. This is demonstrated here for the polar CO molecule. We select CO as our case study because the structure factors for CO (see Ref. [23]) show substantially different emission rates at $\beta = 0$ and $\beta = 180^\circ$. Moreover, both HeH^{2+} and CO have σ -type HOMO orbitals. For the CO molecule, we present data analogous to that for HeH^{2+} in Fig. 2, focusing on ionization yields at orientation $\beta = 0$ employing laser pulses with trapezoidal envelope and CEP

values of 0 and π (we will not consider the minimal asymmetry case where CEP = $-\pi/2$ and $\pi/2$). The yields were calculated for laser pulses with durations ranging from 4 to 15 cycles ($N_{\text{cyc}} = 4-15$), as depicted in Fig. 5(a). Interestingly, even in the regime of longer pulse durations, the ionization yields differ for the two CEPs. We plot the asymmetry as a function of pulse duration (N_{cyc}) in Fig. 5(b), considering peak field strengths of 0.04 a.u. (solid line) and 0.05 a.u. (dotted line). This plot reveals an oscillatory pattern similar to that observed for HeH^{2+} in Fig. 2, with little sensitivity to laser intensity, especially for longer pulses. Additionally, asymmetry is plotted against the field asymmetry $\xi(N_+, N_-)$ for pulses comprising $N_{\text{cyc}} = 4-15$, at field strengths of 0.04 and 0.05 a.u. in Figs. 5(c) and 5(d), respectively. Similar to HeH^{2+} , the asymmetry demonstrates linear relation with $\xi(N_+, N_-)$ and remains largely unaffected by variations in laser intensity as can be seen from the linear regressions in Figs. 5(c) and 5(d).

V. CONCLUSIONS

In this study, we presented TDSE calculations of ionization yields from aligned H_2^+ and oriented HeH^{2+} and CO molecules. For H_2^+ , the ionization yields are reflection symmetric across $\beta = 90^\circ$. For the HeH^{2+} and CO molecules, however, the orientation-resolved ionization yields are not reflection symmetric across $\beta = 90^\circ$: The ionization yields are not matching for each orientation angle $\beta = 0-75^\circ$ and their supplementary angles $180^\circ - \beta$. This asymmetry is found to be sensitive to the pulse duration, gradually diminishing with increasing pulse length. We demonstrate that a simple ionization model based on a tunneling ionization picture and concepts from WFAT [13,14] can qualitatively capture the observed asymmetry trends. For the asymmetry to be observed, two criteria have to be met: The structure factors should be substantially different at orientation angles β and $180^\circ - \beta$, resulting in $\chi(\beta) \neq 0$, and the CEP needs to be set so that the electric field is asymmetric, ensuring that the field asymmetry parameter $\xi(N_+, N_-)$ is not zero.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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