

Alignment- and orientation-dependent strong-field ionization of molecules: Field-induced orbital distortion effects

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The adiabatic strong-field approximation is used to study ionization yields as a function of the angle between the polarization of the external field and molecular axis for CO₂, CO, and OCS molecules. We find that orbital distortion plays an important role in explaining positions and relative strengths of extrema in the yields for both polar and nonpolar molecules, even for molecules with low polarizabilities and at low laser intensities. In particular, we show that for CO₂ the maximum in the ionization yield shifts towards the experimentally measured maximum when accounting for orbital distortion. For the CO molecule, not only is the preferred direction of ionization correctly predicted by the theory, but also the ratio between yields for orientations with the electric field pointing towards C and O ends, respectively. For OCS we find that ionization is more probable when the laser field points from the O end towards the S end than when the field points in the opposite direction.

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I. INTRODUCTION

Strong-field ionization (SFI) is the starting point for many strong-field phenomena, e.g., high-order-harmonic generation and above-threshold ionization, as well as a source of fundamental information about the ionized target [1]. Therefore, investigation of SFI of atoms and molecules has been an aim for research since the first strong laser pulses became available.

After the first demonstration of alignment techniques [2], investigation of ionization of aligned molecules by short intense laser pulses has been of great interest [3–7]. Successful descriptions of experimental data for molecules such as O₂ and N₂ with approximate methods, such as the molecular Ammosov-Delone-Krainov (MO-ADK) formula [3] and the strong-field approximation (SFA) [5,6], brought the community to the conclusion, in agreement with intuition, that the ionization yield reflects the geometric structure of the active orbital. Hence, the ionization yield is minimized when the polarization direction of a driving laser field lies in a nodal plane of the molecular orbital and is maximized when the laser field points towards a large density component of the orbital. Nevertheless, evidence exists showing that this is not always the case and hence indicates a more complex nature of the problem (see, e.g., Ref. [7] for ionization yields of CO₂). Results from calculations based on the time-dependent Schrödinger equation (TDSE) in the single-active-electron (SAE) approximation [8] and time-dependent density-functional theory (TDDFT) [9] brought forward the ideas that coupling of the bound part to the excited-state manifold [8] as well as incorporation of multiple ionic states taking part in the process [10] may be crucial elements in a proper description of SFI from aligned molecules.

More recently, when efficient methods for orienting molecules became available [11–14], a strong interest was also directed towards the investigation of ionization yields from oriented polar molecules [14–18]. Here, similarly to molecules with inversion symmetry, the ionization yield seems to map the orbital structure for many molecules (see, e.g., Ref. [17] for ionization yields of CO and NO). Nevertheless, studies of

the OCS molecule [14,19,20] show, as in the case of nonpolar molecules, that ionization yields do not always reflect the shape of the active orbital and, apart from the strong influence of the Stark shift, the effects of excited states may also be significant. Moreover, it was shown that the influence of different ionic states may be significant at high laser intensities for certain orientation angles (see Refs. [21,22]).

The existing discrepancies between theories and lack of agreement with the experimental data, which will be detailed later, call for more theory investigations to fully understand the process of SFI. In this paper we investigate ionization yields for linearly polarized pulses from aligned and oriented molecules for which the comparison between experiment and theory proved to be controversial, namely, CO₂ [7–9,15,18,23–25], CO [17,18,22,25–28], and OCS [14,16,18–21] molecules. We investigate the influence of field-induced orbital distortion and find it important for SFI. In order to incorporate the orbital distortion we introduce the adiabatic strong-field approximation (ASFA), first considered for high-order-harmonic generation [29,30], for SFI. The method accounts for coupling of the active orbital with the excited states in an adiabatic manner via distortion of the molecular orbital in the external field. This approach can be easily extended to take into account multiple-orbital contributions, within an independent-electron model, by incoherently adding the contributions to the ionization yield for different orbitals. The approach can also be readily applied to larger systems than considered here. We report an essential improvement in comparison with experiments in ionization yields as compared to the predictions of the SFA and Stark-shift corrected SFA (SSFA) [31] methods. In this regard, the results presented for CO₂, CO, and OCS molecules provide insight into the SFI process.

The paper is organized as follows. In Sec. II we briefly introduce the ASFA method for SFI following Ref. [30]. The ionization yields for the ASFA method are presented and compared with SFA and SSFA results for different molecular species in Sec. III. A summary is given in Sec. IV. Atomic units are used throughout unless indicated otherwise.

II. METHODOLOGY

The differential probability for emission of an electron with final momentum \mathbf{k}_f is

$$\frac{dP}{d\mathbf{k}_f} = |\langle \psi_{\mathbf{k}_f}^- | \psi(T) \rangle|^2, \quad (1)$$

where T is some instant of time after the end of the pulse, $|\psi_{\mathbf{k}_f}^- \rangle$ is the scattering state with the asymptotic momentum \mathbf{k}_f , and $|\psi(T) \rangle$ is the wave packet that is formed by the evolution in the external laser pulse. Here we focus on the influence of field-induced distortion of molecular orbitals on ionization yields. Therefore, we turn to the ASFA where the wave packet is subject to a series of approximations [30]. Below we briefly repeat the main findings of the ASFA approach and present its implementation to momentum distributions and, subsequently, ionization yields.

A. Adiabatic strong-field approximation for strong-field ionization

The dynamics of the active orbital represented in the essential state expansion within ASFA [30] is given by

$$|\psi^{\text{ASFA}}(t)\rangle = |\phi_0(t)\rangle \exp\left(-i \int_{t_0}^t E_0(t') dt'\right) + \int d\mathbf{k} c_{\mathbf{k}}^{\text{ASFA}}(t) |\mathbf{k}(t)\rangle, \quad (2)$$

with $|\phi_0(t)\rangle$ the adiabatic ground state, which we refer to as the highest occupied molecular orbital (HOMO) in the following, which solves the time-independent mean-field equation at time t :

$$f(t)|\phi_0(t)\rangle = E_0(t)|\phi_0(t)\rangle, \quad (3)$$

where $f(t)$ is expressed in terms of the Fock operator f_0 and the term $\mathbf{F}(t) \cdot \mathbf{r}$ describing the interaction with the instantaneous electric field and t_0 is some instant of time before the beginning of the pulse. The expansion coefficients are given by

$$c_{\mathbf{k}}^{\text{ASFA}}(t) = i \int_{t_0}^t \langle \mathbf{k}(t') | \mathbf{F}(t') \cdot \mathbf{r} | \phi_0(t') \rangle \times \exp\left(-i \int_{t'}^t E_k(t'') dt'' - i \int_{t_0}^{t'} E_0(t'') dt''\right) dt'. \quad (4)$$

The energy of the bound part can be approximated by

$$E_0(t) = -I_p - \boldsymbol{\mu} \cdot \mathbf{F}(t) - \frac{1}{2} \mathbf{F}(t)^T \underline{\underline{\boldsymbol{\alpha}}} \mathbf{F}(t), \quad (5)$$

with I_p the ionization potential, $\boldsymbol{\mu}$ the permanent dipole moment, and $\underline{\underline{\boldsymbol{\alpha}}}$ the polarizability tensor of the HOMO. In Eqs. (2) and (4), the state

$$|\mathbf{k}(t)\rangle = |\mathbf{k} + \mathbf{A}(t)\rangle \quad (6)$$

is the momentum eigenstate with position representation

$$\langle \mathbf{r} | \mathbf{k}(t) \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}(t) \cdot \mathbf{r}} \quad (7)$$

such that $|\mathbf{k}(t)\rangle \exp[-i \int_0^t E_k(t') dt']$ is the Volkov state with energy

$$E_k(t) = k(t)^2/2 = [\mathbf{k} + \mathbf{A}(t)]^2/2, \quad (8)$$

which solves the Schrödinger equation for a free electron in the presence of the electromagnetic field, where $\mathbf{A}(t) = \int_{-\infty}^t dt' \mathbf{F}(t')$ is the vector potential.

The coefficient $c_{\mathbf{k}}^{\text{ASFA}}(t)$ and the energy of (5) depend on the orientation between the molecule and the direction of the field. To ease notation this dependence was suppressed, but will be specified in the expressions for the observables below.

B. Photoelectron momentum distribution and yields

After inserting the final form of the wave function from Eq. (2) into Eq. (1), replacing $\langle \psi_{\mathbf{k}_f}^- |$ with $\langle \mathbf{k}_f |$ following the SFA approach, and assuming that $\mathbf{A}(t) = 0$ before the beginning and after the end of the pulse, we obtain the differential probability for emission of an electron with final momentum \mathbf{k}_f expressed in ASFA as

$$\frac{dP}{d\mathbf{k}_f}(\beta) = |c_{\mathbf{k}_f}^{\text{ASFA}}(T)|^2, \quad (9)$$

with $c_{\mathbf{k}}^{\text{ASFA}}(T)$ given by Eq. (4). The values of the amplitudes $c_{\mathbf{k}_f}^{\text{ASFA}}(T)$ and therefore also $\frac{dP}{d\mathbf{k}_f}(\beta)$ depend on the orientation between the molecular and the laboratory frames as specified though the three Euler angles. In this work we consider linear molecules and only the angle β between the molecular axis and the polarization direction of the linearly polarized light needs to be specified. The total yield $Y(\beta)$ for a given β is then obtained by integration over the momenta

$$Y(\beta) = \int d\mathbf{k}_f \frac{dP}{d\mathbf{k}_f}(\beta). \quad (10)$$

For SFA and SSFA theories the ket in Eq. (4) is the field-free undistorted HOMO, i.e., for the SFA

$$c_{\mathbf{k}}^{\text{SFA}}(T) = i \int_{t_0}^T \langle \mathbf{k}(t') | \mathbf{F}(t') \cdot \mathbf{r} | \phi_0 \rangle \times \exp\left(-i \int_{t'}^T E_k(t'') dt'' + i I_p t'\right) dt' \quad (11)$$

and for the SSFA [31]

$$c_{\mathbf{k}}^{\text{SSFA}}(T) = i \int_{t_0}^T \langle \mathbf{k}(t') | \mathbf{F}(t') \cdot \mathbf{r} | \phi_0 \rangle \times \exp\left(-i \int_{t'}^T E_k(t'') dt'' - i \int_{t_0}^{t'} E_0(t'') dt''\right) dt', \quad (12)$$

with $E_0(t'')$ given by Eq. (5). The SFA and SSFA results are readily obtained from Eqs. (9) and (10) by replacing $c_{\mathbf{k}_f}^{\text{ASFA}}(T)$ by $c_{\mathbf{k}_f}^{\text{SFA}}(T)$ [Eq. (11)] and $c_{\mathbf{k}_f}^{\text{SSFA}}(T)$ [Eq. (12)], respectively.

III. IONIZATION YIELDS

Here we present ionization yields of CO₂, CO, and OCS for the SFA, SSFA, and ASFA methods obtained by integrating the momentum distribution [see Eqs. (9) and (10)] over the

outgoing electron momenta for a range of alignment and orientation angles β . Calculations were performed for pulse parameters chosen to enable reliable comparison with existing experimental data and will be specified below for the different molecules. All pulses satisfy that the integral over the electric field is vanishing, as it should be for a propagating pulse [32].

The implementation of the ASFA theory requires a calculation of distorted initial orbitals for various instantaneous field values [see Eq. (3)]. These orbitals are obtained using standard quantum chemistry software [33]. We use an augmented correlation-consistent polarized valence triple- ζ (aug-cc-pVTZ) basis set [34,35] for accurate Hartree-Fock (HF) calculations for all SFA, SSFA, and ASFA methods. The nuclei for each molecule were placed at the experimental equilibrium distance given by the NIST Computational Chemistry Comparison and Benchmark Database [36]. The vibrational energies for the considered molecules are fractions of an eV. The highest vibrational energy is for CO and equals 0.269 eV [36]. The corresponding time scale is then $\simeq 15.4$ fs. The fastest vibrational time scales for CO₂ and OCS are $\simeq 22$ fs and $\simeq 16$ fs, respectively. The pulse durations are ~ 7.5 fs for CO, ~ 12 fs for CO₂ and ~ 7.5 fs for OCS. Hence, we expect it to be accurate to consider the nuclei frozen and fixed at their equilibrium positions during the electron dynamics. The remaining data required for acquiring the ionization yields, i.e., ionization potential, permanent dipole moment, and polarizability of the HOMO for each molecule, were calculated based on these internuclear distances. We focus our analysis on the results obtained from the HOMO. For the case of degenerate HOMOs of π symmetry (CO₂ and OCS), ionization yields are obtained by adding contributions from each degenerate HOMO incoherently.

A. The CO₂ molecule

It is well known that the SFA-based theory, the MO-ADK theory, and the weak-field asymptotic theory (WFAT) [18,25,37] fail to predict the experimental position of the maximum in the alignment-dependent ionization yield. Experimentally, the maximum was measured to be at $\beta = 45^\circ$ [7,15]. A maximum is exhibited by the SFA and SSFA at around $\beta = 33^\circ$ (see, e.g., [23] and Fig. 1), by the MO-ADK theory at $\beta = 25^\circ$ (see [7]), and by the WFAT at $\beta = 39^\circ$ [18]. It has been pointed out that, solving the TDSE in the SAE approximation [8], the dynamics in the excited-state manifold plays a crucial role in explaining the position of the maximum. In both SFA-based and tunneling theories such coupling is disregarded, which is hence a possible source of discrepancy with experimental data. We note that other approaches have been successful in calculating the position of the maximum, e.g., TDSE based calculations [8], TDDFT [9], and a tunneling theory where the correct position of the maximum was attributed to the interplay between position- and momentum-space properties of the active orbital in tunneling ionization [24].

Like all others, our calculations for the CO₂ molecule were obtained for frozen nuclei. The distance between O and C atoms was set to be 2.196 and the ionization potential was calculated to be $I_p = 0.544$. The polarizability tensor in the molecular fixed frame was diagonal with $\alpha_{xx} = 2.454$,

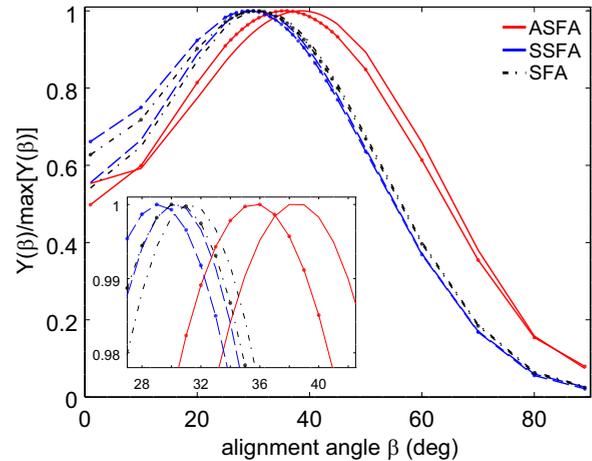


FIG. 1. (Color online) Ionization yield $Y(\beta)$ for CO₂ as a function of the alignment angle β . The yield is normalized to the maximum yield for each method. Bare lines show results for the peak intensity 0.3×10^{14} W/cm² and lines with dots show results for the peak intensity 1.1×10^{14} W/cm². See the text for more laser parameters.

$\alpha_{yy} = 3.846$, and $\alpha_{zz} = -1.979$ for the HOMO with the nodal plane perpendicular to the laser polarization direction and $\alpha_{xx} = 3.846$, $\alpha_{yy} = 2.454$, and $\alpha_{zz} = -1.979$ for the HOMO with the nodal plane parallel to the laser polarization direction; the permanent dipole moment was $\mathbf{0}$.

Figure 1 depicts ionization yields normalized to the highest value of the yield for each method as a function of the alignment angle β for the molecule exposed to a five-cycle, linearly polarized, laser pulse with a flat-top envelope, and intensities 0.3×10^{14} W/cm² with a 800-nm wavelength and 1.1×10^{14} W/cm² with a 820-nm wavelength to connect to the existing experimental data ([15] and [7], respectively). As seen from the figure, the SFA results predict the maximum around $\beta = 31^\circ$ (for $I = 0.3 \times 10^{14}$ W/cm²) and $\beta = 30^\circ$ (for $I = 1.1 \times 10^{14}$ W/cm²). The correction from the Stark shift, which originates from the nonvanishing polarizability [see Eq. (5)], shifts the maximum to even lower angles ($\beta = 30^\circ$ and 29° , respectively). These results agree with the former applications of SFA for ionization from CO₂ and there is a large disagreement with the experimental data. Only after the orbital distortion is accounted for (in the ASFA) does the maximum shift to higher angles yielding a maximum around $\beta = 39^\circ$ for the lower intensity and $\beta = 36^\circ$ for the higher intensity, which is a significant improvement. A possible reason for the shift of the maximum from a higher to a lower angle with increasing intensity could be the following. The low-intensity laser pulse may populate field-free states, as included via the adiabatic ansatz, for which the yield is maximized for higher angles with larger probability, whereas the high-intensity pulse may induce transitions to states for which the yields peak at lower angles. In any case, the observed effect is in agreement with the conclusions from Ref. [8], namely, that the maximum is shifting due to the fact that ASFA takes into account excitations via orbital distortion and in that way the dynamics in the excited-state manifold is partly accounted for. The ASFA results, though not in the perfect agreement with the experimental data, show the importance of accounting

for orbital distortion even for a molecule such as CO_2 with relatively low polarizability.

B. The CO molecule

We now turn our attention to the CO molecule for which a number of experiments investigating SFI by both circularly [27] and linearly [17,26] polarized pulses have been performed. All the experimental results agree that the electrons are more easy to detach when the external field has a component pointing from the C to the O end, hence the electron leaves preferably from the C end. Theory, on the other hand, is not that unanimous. While the SFA and SSFA, as well as the MO-ADK theory, agree that it is easier to ionize the molecule from the C end [17], for tunneling theories that account for the Stark shift, i.e., the WFAT and Stark-shift corrected MO-ADK theory, the opposite trend of the yield with β was found [17,18,25]. That is, the prediction is that the electrons are more likely to detach when the field points from the O end to the C end.

Here we apply ASFA theory to investigate this discrepancy further. We freeze the molecule on the z axis such that $z[\text{O}] = 1.859$ and $z[\text{C}] = -0.274$. The ionization potential is calculated to be $I_p = 0.555$. In the molecular fixed frame, the permanent dipole moment for the HOMO is $\mu_z = 1.141$ and the diagonal elements of the polarizability tensor $\alpha_{xx} = \alpha_{yy} = 3.811$ and $\alpha_{zz} = 3.550$.

Numerical results for ionization yields normalized to the highest value of the yield for each method as a function of the orientation angle β for a linearly polarized three-cycle laser pulse with a \sin^2 envelope [see Fig. 2(c)], 2×10^{14} W/cm² peak intensity, and 800-nm wavelength for SFA, SSFA, and ASFA methods are depicted in Fig. 2(a). For $\beta = 0^\circ$ the maximum of the field points towards the O end [see Fig. 2(b)]. The SFA and SSFA results shown are in qualitative agreement with published results [17]. Both these methods predict correctly, in comparison to experimental data, that it is easier to ionize the molecule from the C end (field points from C towards O, $\beta = 0^\circ$) than from the O end (field points from O towards C, $\beta = 180^\circ$). The asymmetry, defined as $w = [Y(\beta = 0^\circ) - Y(\beta = 180^\circ)]/[Y(\beta = 0^\circ) + Y(\beta = 180^\circ)]$, where $Y(\beta)$ is the ionization yield, is strongly overestimated by the SFA method compared to the experimental value estimated to be around 0.30 [17], whereas the asymmetry determined by the SSFA

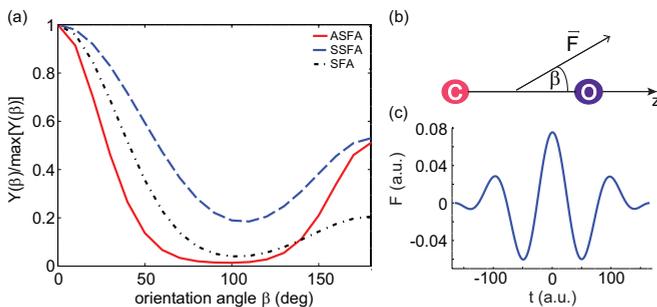


FIG. 2. (Color online) (a) Ionization yield $Y(\beta)$ for CO as a function of the orientation angle, normalized to the maximum yield for each method. See the text for laser parameters. (b) Orientation of the molecule and the laser field. (c) Laser pulse used.

method is $w = 0.31$. The results for the ASFA method, similarly to SSFA, not only predict correctly the preferred ionization direction, but also the asymmetry is in very close agreement with the experiment, $w = 0.32$. Moreover, the ASFA predicts a much deeper and broader minimum around $\beta = 100^\circ$ than the other two approaches.

We note that a time-dependent Hartree-Fock calculation [28] gave results similar to the ASFA. A TDDFT study reported almost unchanged ionization going from $\beta = 0^\circ$ to $\beta = 180^\circ$ for a laser pulse containing more than five optical cycles and with intensities 3.5×10^{14} W/cm² and larger [22].

C. The OCS molecule

In the case of the OCS molecule, experiments and theory for circularly [14,16] and linearly [18–20] polarized laser pulses show ambiguous results. For circularly polarized light both experiments and theory agree that ionization takes place more readily for the laser field pointing towards the S end and electrons detaching from the O end. For linearly polarized pulses there is experimental evidence that the electron is most likely to be detached from the S end [20], whereas another experiment indicates that the highest probability for electron ejection is when the laser field points in a direction perpendicular to the internuclear axis [19].

For the OCS calculations the molecule was placed as follows: $z[\text{S}] = -1.970$, $z[\text{C}] = 0.990$, and $z[\text{O}] = 3.198$; for the HOMO the ionization potential was calculated to be $I_p = 0.416$. In the molecular fixed frame the permanent dipole moment of the HOMO was $\mu_z = 0.615$ and the polarizability was $\alpha_{xx} = 8.964$, $\alpha_{yy} = 7.764$, and $\alpha_{zz} = 10.116$ for the HOMO with the nodal plane perpendicular to the laser polarization direction and $\alpha_{xx} = 7.764$, $\alpha_{yy} = 8.964$, and $\alpha_{zz} = 10.116$ for the HOMO with the nodal plane parallel to the laser polarization direction.

A comparison of the ionization yields normalized to the highest value of the yield for each method for OCS molecule exposed to a short, three-cycle, linearly polarized laser pulse with a \sin^2 envelope [see Fig. 3(c)], 800-nm central wavelength, and intensity 7×10^{13} W/cm² for the SFA, SSFA, and ASFA methods is depicted in Fig. 3(a). The SFA and SSFA curves have their global maxima at around $\beta = 35^\circ$. The correction due to the Stark shift shifts the peak to slightly larger angles in comparison to the SFA method. Another, local,

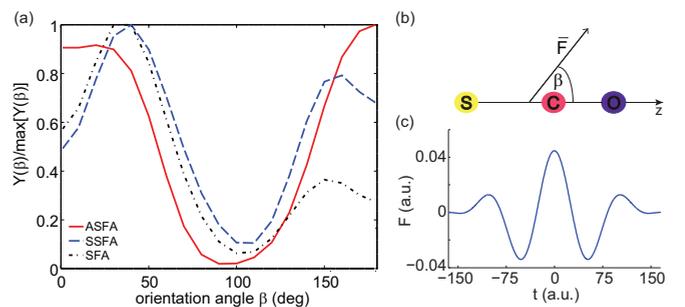


FIG. 3. (Color online) (a) Ionization yields $Y(\beta)$ for OCS as a function of the orientation angle normalized to the maximum yield for each method. See the text for laser parameters. (b) Orientation of the molecule and the laser field. (c) Laser pulse used.

maximum is present at around $\beta = 155^\circ$ for both curves. The structure of these curves maps out the geometrical shape of the ionizing orbital in disagreement with the experimental results for linearly polarized laser pulse that we are aware of [19,20]. This indicates that, apart from the role of the orbital shape, other phenomena may be of importance, i.e., rescattering electrons, the Stark shift, the dynamics in the excited-state manifold, and different ionic states, as it was alluded to earlier [19].

The ASFA, on the other hand, predicts that the most favorable orientation angle for electrons to detach is for the laser field pointing towards the S end yielding a peak for $\beta = 180^\circ$. This is in agreement with the experimental data [14,16] that show a preference for ionization from the O end. The peak seen at $\beta = 35^\circ$ for SFA and SSFA is not present for ASFA data. Instead, a broad local maximum around $\beta = 15^\circ$ is present. This difference suggests that dynamics in the excited-state manifold accounted for via the adiabatic ground state plays an important role, similarly to the CO₂ case. For OCS, a study of the contributions to the ionization yield at low β angles from the two degenerate HOMOs revealed that these contributions are higher for both orbitals (relative to the maximum value of the yield for each method) in the case of the ASFA method than in the other approximations, while the maximum at around 40° , a feature of the yield originating from the HOMO with the nodal plane perpendicular to the laser polarization, is of similar magnitude and position in the ASFA, SSFA, and SFA. The incoherent sum of the contributions from both degenerate HOMOs results in a distinct peak with the SSFA and SFA methods and in a yield that is relatively insensitive to the value of β up to around 30° for the ASFA approach. For CO₂ the magnitude of the yields from the HOMOs in the ASFA, SSFA, and SFA are similar and only the shift in the peak position is observed (Fig. 1).

Note that the measurements in Ref. [19], i.e., ionization by linearly polarized pulses for the alignment-dependent ionization yield in OCS, show a maximum when the ionizing field is perpendicular to the internuclear axis. This behavior cannot be explained by the role of the excited states as it was suggested previously [18,19]. Since in our method only a direct ionization is accounted for, our analysis does not rule out the

rescattering process as a possible explanation for the yields measured in [19].

We also note that the TDDFT calculation [21] has shown a strong influence of orbitals more tightly bound than the HOMO, at intensities five times higher than used in this work. Moreover, it was pointed out that the ionization yield maps out the Kohn-Sham orbital, rather than its HF counterpart.

IV. CONCLUSION

We presented the ASFA method for SFI to account for field-induced orbital distortion of the molecular target. Results calculated for CO₂, CO, and OCS molecules show an overall improvement as compared to SFA and SSFA methods, indicating that the dynamics in the excited-state manifold plays an important role during the ionization process. Even for molecules with low polarizabilities exposed to relatively low intensity, lasers may lead to the observation of orbital distortion effects. In particular, we showed that taking into account field-induced orbital distortion shifts the maximum of the ionization yield for CO₂ molecule to higher angles than obtained from theories neglecting the distortion, towards the experimentally measured position. Moreover, not only did the evaluated ionization yields for ionization of CO correctly predict that it is more probable for electron to get detached from the C end than from the O end, but also the calculated asymmetry agrees with the experiment. Finally, as an example of application of the method to a triatomic polar molecule, calculations for OCS showed that the most favorable orientation angle for a molecule to ionize is when the laser field points from the O end towards the S end.

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