

Strong-field ionization of polar molecules: Stark-shift-corrected strong-field approximation

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We extend the molecular strong-field approximation for ionization, in the tunneling limit, to include systematically the linear and quadratic static Stark shifts of the ionizing molecular orbital. This approach, simple to implement, is capable of describing the essential physics of the process of strong-field ionization of oriented polar molecules by circularly polarized laser pulses. The modification of the molecular orbitals in strong fields is also discussed and in cases of extreme polarization of inner electrons a simple model is devised. We find very good agreement between the results from our model and those obtained in the recent experiment on ionization of oriented carbonyl sulphide and benzonitrile molecules [L. Holmegaard *et al.*, *Nature Phys.* **6**, 428 (2010)].

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I. INTRODUCTION

Obtaining molecular-frame ionization cross sections from aligned and oriented molecules [1] not only advances the knowledge on strong-field processes, but also carries information on the orbital structure [2,3]. The detailed knowledge of the ionization dynamics in strong fields can then, for example, be used to obtain insight into the time-dependent electronic dynamics for larger systems in experiments employing the femtosecond-attosecond pump probe techniques [4].

The experiments on ionization from aligned or oriented molecules can be broadly divided into two types. The first type of experiments are relying on the cold target recoil ion momentum spectrometer (COLTRIMS) [5] technique that enables kinematically complete experiments where the orientation of the molecule in space prior to the interaction with the laser field is inferred from the recorded dissociated molecular fragments after the end of the interaction [2,6–13]. Mapping of the initial orientation of the molecule before the interaction is possible only by isolating a particular dissociation channel of the molecule. Since dissociation channels of larger molecules are not well known, these experiments are usually restricted to smaller molecules.

The second type of experiments confine the molecules in space prior to the interaction with the laser field. The first experiments of that type were conducted on aligned linear molecules [14–16]. Making use of the large polarizabilities and dipole moments of the target molecules, it is possible to adiabatically orient them with a fixed head-to-tail ratio [17] before the interaction with the strong-field laser pulse [3]. This opens up possibilities for investigating photoelectron angular distribution in the molecular fixed frame. These distributions carry much more information than the corresponding signal from a nonoriented sample. For example, the effect of the molecular dipole moments and polarizabilities on the ionization dynamics of the probed molecules can be investigated in detail. In this paper we restrict ourselves to the description of these experiments, investigating the influence of the Stark shifts due to large permanent dipole moments and polarizabilities of the target molecules on the initial ionization step.

Theoretically, in order to fully account for the ionization of molecules in strong laser fields, one has to solve the

time-dependent Schrödinger equation in its full dimensionality. This is, however, an extremely complicated task, only possible for the most simple molecules. Luckily semianalytical models, providing the basic physical insight, are available. A very popular tool, in this respect, is the molecular strong-field approximation (MO SFA) [18–20], which is a generalization of the atomic strong-field approximation (SFA) pioneered by Keldysh [21] (see also [22,23]). In SFA and MO SFA, single ionization is modeled as a transition from an initial field-free state to a Volkov state, which is the wave function for an electron in an electromagnetic field. Hence, intermediate bound states and the Coulomb interaction in the final state are completely neglected. Another widely used model for description of ionization of molecules in strong fields is the molecular tunneling theory [the molecular Ammosov-Delone-Krainov (MO-ADK) theory] [24], which is an extension of the atomic tunneling theory (ADK) [25,26]. The molecular extensions of both ADK and the SFA take into account the shape (the geometry) of the initial molecular orbital.

Ionizing oriented molecules that possess large dipole moments and polarizabilities with strong laser pulses induces, however, large Stark shifts of the energy levels and hence leads to large modulations of the ionization potential. Due to the Stark shift, ionization of such molecules gives rise to phenomena (e.g., strong suppression of the ionization signal in specific regions of momentum space) not seen in the nonpolar case [3]. The standard formulation of the MO SFA does not account for the Stark shift of polar molecules. This motivates the development of Stark-shift corrections to the MO SFA that preserves the simplicity of the approach and, at the same time, captures the essential physics.

In this paper, we present a simplified, but yet systematic, way to approximatively Stark-shift correct the length gauge MO SFA in the tunneling limit. We restrict ourselves to the case of ionization of oriented molecules by circularly polarized laser pulses where the rescattering-induced postionization interaction with the molecular core is limited. In addition, we discuss the modification of the molecular orbitals by slowly varying strong fields. The performance of the corrected MO SFA is illustrated by calculating the photoelectron momentum distributions (PADs) for strong-field ionization of

oriented carbonyl sulphide (OCS) and benzonitrile (C_7H_5N) molecules by a circularly polarized laser field. The distributions show, when compared with results obtained using the standard MO SFA, striking effects of the field-dependent modulation of the ionization potential due to the Stark shift. Furthermore, our results are shown to be in very good agreement with results from a previous experiment and tunneling calculations [3], thus, validating the proposed method for calculating the ionization of polar molecules to strong external fields in the tunneling limit.

This paper is organized as follows. In Sec. II we discuss the Stark shifts in the static-field limit. In Sec. III a way to approximatively Stark-shift correct the length gauge MO SFA in the adiabatic limit is presented. In Sec. IV we discuss the modification of the molecular orbitals due to the polarizability, and illustrate the proposed method by strong-field calculations on OCS and C_7H_5N . In Sec. V we present the conclusion. Atomic units ($\hbar = a_0 = m_e = 1$) are used throughout, unless stated otherwise.

II. STATIC STARK SHIFTS

In general, the ionization potential I_p of a molecular system is defined as the difference between the total energy of the molecular ion and the corresponding neutral. In weak static fields the total energy of the ion and the neutral do not change substantially; however, for polar molecules and in strong fields the change of the total energy of the neutral and its unrelaxed cation can be very substantial. Note that we refer to the total energy of the unrelaxed ion, ignoring a possible difference of the dipole moments and polarizabilities of the ionic species obtained through different ionization channels. The unrelaxed cation is considered because the electron dynamics occurs on a time scale where the nuclei have not had time to move. The total energy of a molecule (M) and its unrelaxed cation (I) E^{M-I} is a function of the static field \mathbf{F} . To second order in field strength, the total energy of the molecule and cation $E^{M-I}(\mathbf{F})$ is given by (see, e.g., [27])

$$E^{M-I}(\mathbf{F}) = E^{M-I}(0) - \boldsymbol{\mu}^{M-I} \cdot \mathbf{F} - \frac{1}{2} \mathbf{F}^T \boldsymbol{\alpha}^{M-I} \mathbf{F}, \quad (1)$$

where $\boldsymbol{\mu}^{M-I}$ is the dipole moment, $\boldsymbol{\alpha}^{M-I}$ is the polarizability tensor, and $E^{M-I}(0)$ is the field-free total energy of the system. The superscripts M and I refer to the molecule and the molecular cation, respectively. Since the molecule and the cation do not have identical permanent dipole moments and polarizabilities, the ionization potential $I_p = E^I - E^M$ becomes

$$I_p(\mathbf{F}) = I_p(0) + \Delta\boldsymbol{\mu} \cdot \mathbf{F} + \frac{1}{2} \mathbf{F}^T \Delta\boldsymbol{\alpha} \mathbf{F}, \quad (2)$$

where

$$\Delta\boldsymbol{\mu} = \boldsymbol{\mu}^M - \boldsymbol{\mu}^I, \quad \Delta\boldsymbol{\alpha} = \boldsymbol{\alpha}^M - \boldsymbol{\alpha}^I. \quad (3)$$

Equations (2) and (3) show very explicitly that the ionization potential depends not only on the magnitude of the electric field vector \mathbf{F} but also on the angles of the field orientation with respect to the main polarizability axes and the permanent dipole of the molecule. An alternative but equivalent way of formulating the shift of the ionization potential is to introduce the dipole moment and polarizability associated with the orbital that participates actively in the ionization process.

The previous considerations were recently incorporated into a Stark-shift-corrected tunneling model that explained the experimental results on strong-field ionization of one-dimensionally oriented OCS molecules [3]. While this model gave satisfactory results, it did not account for two important points. The first point is that in a tunneling model the coherence of the wave packet is lost, and obviously any interference effect of the ionized electron wave packet is absent. The second point concerns the situations in which a molecule is oriented so that the electric field vector lies in the nodal plane of the ionizing molecular orbital. In this case the emission along the field direction is forbidden due to symmetry reasons. However, the standard ADK tunneling theory, as well as MO-ADK theory, assumes that the tunneling occurs exactly opposite to the field direction [24,25], which breaks down for fields lying in the nodal plane of the ionizing orbital. In the tunneling theory the momentum distribution, at emission, transverse to the electric field direction is proportional to $\exp[-p_\perp^2 \sqrt{2I_p}/F(t)]$ [28], where p_\perp is the momentum of the electron transverse to the instantaneous field direction. This is obviously not true when the electric field vector lies in the nodal plane of the molecule. Therefore, to obtain fair agreement with recent experimental data on three-dimensionally oriented C_7H_5N , an *ad hoc* dressing of the preexponential factor of the tunneling amplitude was performed in Ref. [3], taking the transverse momentum distribution at the birth of the electron coinciding with the simplest orbital that has a nodal plane in the same direction. The MO SFA, on the other hand, even without accounting for the Stark shifts, automatically accounts for the existence of the nodal plane structures in the molecular orbitals [29,30]. Therefore, by correcting the usual MO SFA for the Stark-shift one would obtain a model that accounts both for the static Stark shifts and the nodal planes of the molecular orbitals.

The standard length gauge SFA for atoms has a common limit with tunneling result for static fields [31] as was explicitly shown for the case of the zero-range potential [32]. Therefore, as we will see, the Stark shift of the ionization potential (2) enters the SFA formalism by employing the adiabatic ansatz. Below we give the derivation of the corrected MO SFA to account for the Stark shifts. We stress that the applicability of our Stark-shifted MO SFA is restricted to the tunneling limit, that is, Keldysh parameter [21] $\gamma = \omega \sqrt{2I_p}/F < 1$. Beyond the tunneling limit, the correction based on static Stark shifts would fail since then the field cannot be regarded as quasistatic. All the examples of strong-field ionization of oriented polar molecules considered here are in or very close to the tunneling regime.

III. STARK-CORRECTED LENGTH GAUGE MO SFA

We start the derivation from the time-dependent Schrödinger equation (TDSE) governing the dynamics of the molecular system interacting with the laser field,

$$i \partial_t \Psi(t) = [H_0 + V(t)] \Psi(t), \quad (4)$$

where H_0 is the field-free Hamiltonian and $V(t) = \sum_{j=1}^n \mathbf{r}_j \cdot \mathbf{F}(t)$ denotes the interaction of the n -electron system with the

electric field of the laser pulse. This partial differential equation is equivalent to the following integral equation:

$$\Psi(t) = -i \int_0^t U(t,t')V(t')U_0(t',0)\Phi_0 dt' + U_0(t,0)\Phi_0, \quad (5)$$

given the initial condition $\Psi(0) = \Phi_0(0)$, where Φ_0 is an eigenstate of the field-free Hamiltonian, U , $i\partial_t U(t,t_0) = [H_0 + V(t)]U(t,t_0)$, is the time-evolution operator for the total system and U_0 , $i\partial_t U_0(t,t_0) = H_0 U_0(t,t_0)$, is the time-evolution operator for the field-free system. The transition amplitude to a final state $|\Psi_f(t)\rangle$ is

$$T_{fi} = -i \int_0^\tau \langle \Psi_f(t) | V(t) | \Phi_0(t) \rangle dt, \quad (6)$$

with τ the pulse duration and Ψ_f the wave function for the liberated electron and the residual ion. Here, we restrict to the case of single ionization and to the independent particle model of the system, so we approximate the initial n -electron wave function by a Slater determinant,

$$\Phi_0(t) = \frac{1}{\sqrt{n!}} \det|\phi_1(\mathbf{r}_1) \cdots \phi_n(\mathbf{r}_n)| \exp[-iE^M(0)t], \quad (7)$$

where ϕ_i and \mathbf{r}_i refer to the i th electron orbital and coordinate, respectively. Next, we concentrate on the channel leading to ionization of the, say, n th electron. In the SFA [21–23,33] we neglect the interaction between the liberated electron and the cation in the final state. Hence, the final state is given by

$$\Psi_f(t) = \frac{1}{\sqrt{n!}} \det|\phi_1(\mathbf{r}_1) \cdots \psi_n^{\mathbf{q}}(\mathbf{r}_n, t)| \exp[-iE^I(0)t], \quad (8)$$

where $\psi_n^{\mathbf{q}}(\mathbf{r}_n, t)$ denotes a Volkov wave function with asymptotic momentum \mathbf{q} . Combining these expressions with Eq. (6), and ignoring the nonorthogonality of the continuum final state orbital with the bound state orbitals, we obtain [19,20]

$$T_{fi} = -i \int_0^\tau \langle \psi_n^{\mathbf{q}}(\mathbf{r}_n, t) | \mathbf{r}_n \cdot \mathbf{F}(t) | \phi_n(\mathbf{r}_n, t) \rangle \exp[iI_p(0)t] dt, \quad (9)$$

which is the key result in the length gauge MO SFA.

In the static field limit, it is possible to modify the above simple derivation to include the adiabatic ansatz in the initial and the final state. Hence, if we assume that both the cation and the neutral, before ionization, are affected adiabatically by the electric field Eqs. (7) and (8) are changed as

$$\Phi_0(t) = \frac{1}{\sqrt{n!}} \det|\phi_1(\mathbf{r}_1, \mathbf{F}(t)) \cdots \phi_n(\mathbf{r}_n, \mathbf{F}(t))| \times \exp\left(-i \int_0^t E^M(\mathbf{F}(t')) dt'\right), \quad (10)$$

$$\Psi_f(t) = \frac{1}{\sqrt{n!}} \det|\phi_1(\mathbf{r}_1, \mathbf{F}(t)) \cdots \psi_n^{\mathbf{q}}(\mathbf{r}_n, t)| \times \exp\left(-i \int_0^t E^I(\mathbf{F}(t')) dt'\right). \quad (11)$$

The adiabatic approximation is valid provided that $\omega \ll I_p(\mathbf{F}(t))$. The cation in question is even more tightly bound than the neutral and, hence, if $\omega \ll I_p(\mathbf{F}(t))$ then $\omega \ll I_p^I$, where I_p^I is the ionization potential of the cation. In the previous equations, in addition to the modification of the total

energy of the molecule and the ion due to the instantaneous amplitude of the field according to (1), we have indicated the distortion of the bound orbitals by the static field, which we will discuss later.

Combining Eqs. (10) and (11) with Eq. (6), the transition amplitude becomes

$$T_{fi} = -i \int_0^\tau \langle \psi_n^{\mathbf{q}}(\mathbf{r}_n, t) | \mathbf{r}_n \cdot \mathbf{F}(t) | \phi_n(\mathbf{r}_n, \mathbf{F}(t)) \rangle \times \exp\left(i \int_0^t I_p(\mathbf{F}(t')) dt'\right) dt, \quad (12)$$

with the exponent given by Eq. (2). Since we would be concerned with examples where the amplitude of the laser pulse is large and the pulse durations are not too short, the saddle-point integration of Eq. (12) yields an identical result as performing the exact time integration [34]. The standard technique of saddle-point integration is used; see the appendix.

In the saddle-point formulation of the SFA, the initial-state symmetry appears in the pre-exponential factor, while the binding energy appears as an argument in the exponential; see Eq. (31) in the Appendix. Any modification of the orbital caused by the field would have an effect on the preexponential factor; this is also the case in the MO-ADK theory [24], where initial orbital symmetry appears in the preexponential factor. In Eq. (12) the initial orbital is a function of the field strength (i.e., it changes adiabatically depending on the field orientation). It is, in general, very hard to account dynamically for such changes of the orbitals, but it is also clear that in the case of very large polarizabilities it is not accurate to use the field-free ones. We discuss the dynamic modification of the orbitals in strong laser fields in the next section.

IV. APPLICATION OF STARK-SHIFT-CORRECTED MO SFA

A. Definitions and considered geometry

We consider strong-field ionization of polar molecules by a circularly polarized laser field. Specifically, we consider a left circularly polarized (LCP) laser pulse, defined in terms of the vector potential $\mathbf{A}(t)$ having a sine squared envelope and polarization in the (y,z) plane,

$$\mathbf{A}(t) = A_0 f(t) \begin{pmatrix} 0 \\ \sin(\omega_0 t + \phi) \sin\left(\frac{\epsilon}{2}\right) \\ \cos(\omega_0 t + \phi) \cos\left(\frac{\epsilon}{2}\right) \end{pmatrix}. \quad (13)$$

In the previous equation, A_0 is the amplitude, ω_0 the central frequency, ϕ the carrier-envelope phase (CEP), $\epsilon = \pi/2$ the ellipticity, and $f(t) = \sin^2\left(\frac{\omega_0 t}{2N}\right)$ the envelope, with N the number of optical cycles. In all calculations presented here, we use long pulses so that the results do not depend on the CEP. The electric field of the laser pulse is obtained from the vector potential as $\mathbf{F}(t) = -\partial_t \mathbf{A}(t)$, so that for LCP $\mathbf{A}(t)$ precedes $\mathbf{F}(t)$ in space (see Fig. 1).

In the following, we give examples of strong-field ionization of oriented polar molecules that are compatible with the experimental setup described in Ref. [3] and sketched in Fig. 1. The target molecules are oriented so that the permanent dipole moment of the molecule $\boldsymbol{\mu}^M$ is antiparallel to the positive z axis, the momentum distributions are recorded on a screen

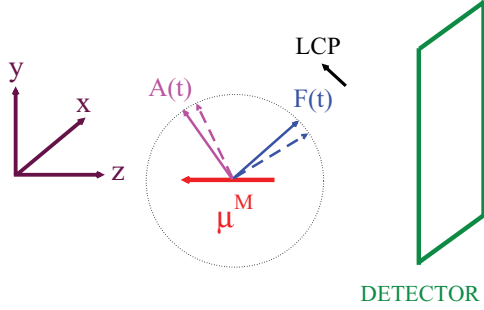


FIG. 1. (Color online) Sketch of the experimental geometry that is considered in the present calculations. See text for details.

perpendicular to the z axis [i.e., the screen is in the (x, y) plane (see Fig. 1)], and the origin of the space-fixed axes (x, y, z) is the center of mass of the molecule. In this setup, disregarding the influence of the molecular potential after the electron emission, that is, using the simple-man model [35], the electron emitted at time t_0 will gain final momentum,

$$\mathbf{q} = -\int_{t_0}^{\infty} \mathbf{F}(t) dt = -\mathbf{A}(t_0). \quad (14)$$

We assume that the laser pulse is relatively long and that it is switched off adiabatically, so that the CEP ϕ does not have influence on the result and the phase difference (and also the spatial angle) between $\mathbf{A}(t)$ and $\mathbf{F}(t)$ amounts to $\pi/2$. According to Eq. (14), to obtain a final momentum \mathbf{q} that has a maximal y component q_y , the electron should tunnel out at time t_0 when the vector potential $\mathbf{A}(t_0)$ is perpendicular to the permanent dipole moment of the molecule $\boldsymbol{\mu}^M$ [i.e., at times when $\mathbf{F}(t_0)$ is parallel or antiparallel to $\boldsymbol{\mu}^M$]. Specifically, when $\mathbf{A}(t_0)$ points in the positive y axis, $\mathbf{F}(t_0)$ points in the positive z axis, emission occurs opposite from the field direction (in the direction of the negative z axis), and the final momentum will have a negative y component ($q_y < 0$). In case $\mathbf{A}(t_0)$ points in the direction of the negative y axis, the emission occurs in the direction of the positive z axis and the final momentum has a positive y component ($q_y > 0$).

The permanent dipole moments and polarizabilities of the molecule and its cation for OCS and C_7H_5N used here are given in the supplementary information to Ref. [3].

B. Standard MO SFA result

First, we turn to the case of strong-field ionization of the OCS molecule by LCP light. To perform calculations within the standard MO SFA, the asymptotic properties of the HOMO, which is degenerate for OCS (see supplementary information to Ref. [3]), are needed. We assume that one of the HOMOs is in the laser polarization (y, z) plane and the other is perpendicular to it [i.e., is in the (x, z) plane]. The two degenerate and orthogonal HOMOs, obtained using the standard GAMESS code [36], are fitted to the asymptotic form of the field-free wave function at large distances,

$$\phi_n(\mathbf{r}) \approx r^{\frac{Z}{\kappa}-1} \exp(-\kappa r) \sum_{lm} C_{lm} Y_{lm}(\hat{\mathbf{r}}), \quad (15)$$

where $\kappa = \sqrt{2I_p(0)}$ and Z is the ionic charge, thereby calculating the coefficients C_{lm} for both orbitals [37].

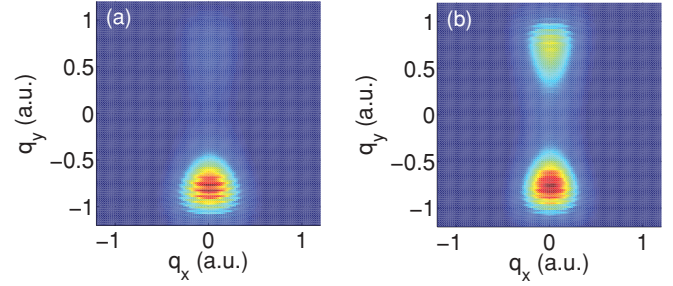


FIG. 2. (Color online) Photoelectron momentum distributions, $\partial^2 P / \partial q_x \partial q_y = \int (\partial^3 P / \partial q_x \partial q_y \partial q_z) dq_z$, for the ionization of OCS, one-dimensionally oriented such that the O-end points in the positive z direction. The laser parameters are as follows: frequency $\omega = 0.057$ (800 nm), peak intensity $I = 2.44 \times 10^{14} \text{ W/cm}^2$, number of optical cycles $N = 10$, and CEP $\phi = 0$. The distribution (a) is obtained using the standard length MO SFA, while the distribution (b) is obtained by including the Stark shift in the exponent [i.e., using Eq. (12)]. Linear color scale is used.

Figure 2 shows the standard length gauge MO SFA momentum distribution [Fig. 2(a)], $\partial^2 P / \partial q_x \partial q_y$, as well as the Stark-shift-corrected [Eq. (12)] momentum distribution [Fig. 2(b)] for the ionization of a one-dimensional (1D) aligned and oriented OCS with the following parameters: 800 nm, peak intensity $I = 2.44 \times 10^{14} \text{ W/cm}^2$, $N = 10$, and CEP $\phi = 0$. The OCS is aligned along the z axis and oriented in such a way that the O end points in the positive z direction. The momentum distributions in Fig. 2 include the combined response of both HOMOs of OCS, obtained by incoherently adding the momentum distributions originating from each of the degenerate HOMOs. The contribution from the (x, z) plane HOMO in the momentum distributions in Fig. 2 is dwarfed by the contribution from the (y, z) plane HOMO because the nodal plane of the former orbital coincides with the laser polarization plane and therefore the ionization from that orbital is suppressed. Below we restrict the discussion to the (y, z) plane orbital and simply refer to it as ‘‘HOMO.’’

The standard MO SFA produces a distribution with a larger probability for ionization with $q_y < 0$ compared to $q_y > 0$. This can be understood from the previous discussion within the simple-man model and by looking at the HOMO [see Fig. 3(a)]. Namely, the majority of the charge is situated near the S end, which, in turn, favors ionization when the electric field has a component in the positive z direction (ionization from the S end) compared to the case where the electric has a negative z component (ionization from the O end). Therefore, the structure of the orbital is such that ionization from the S end is favored. For the LCP of Eq. (13), the final momentum [Eq. (14)] corresponding to ionization from the O end would have a positive y component, and conversely, negative y component when the ionization has occurred from the S end of the molecule. This explains why the momentum distribution is larger for $q_y < 0$ compared to $q_y > 0$ in Fig. 2(a).

C. Dynamic modification of molecular orbitals in strong fields

The asymmetry in the momentum distributions in Fig. 2(a) contradicts the asymmetry in the momentum distributions, observed in the experiments [3], where the $q_y < 0$ part of the

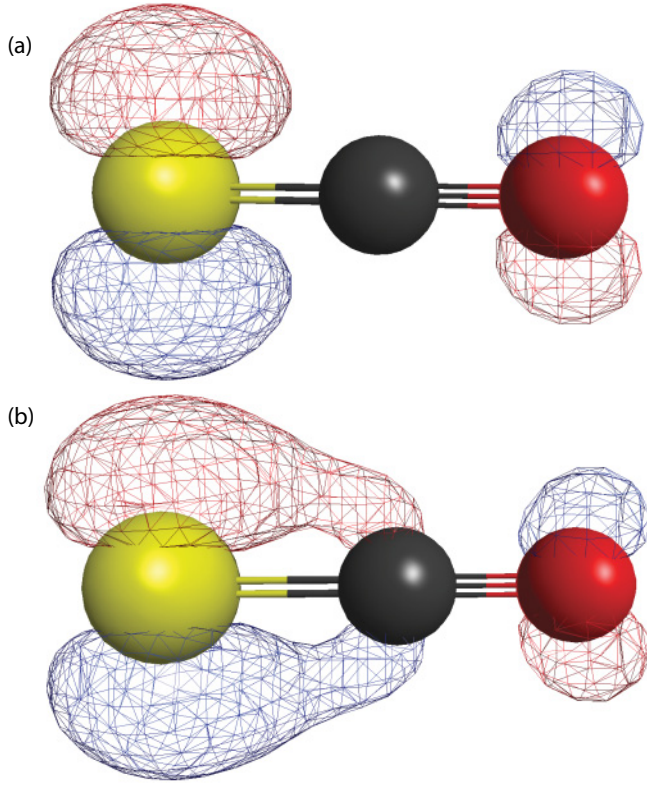


FIG. 3. (Color online) The OCS molecule with the S pointing to the left and the O to the right. The nuclei are at the equilibrium nuclear positions (in a.u.): -2 (sulfur), 0.99 (carbon), and 3.2 (oxygen). (a) Iso-contour of the (y,z) plane HOMO of OCS at spatial points where the norm of the wave function is 0.1 . (b) The same as (a), but now including a static field of magnitude 0.0586 pointing toward the S end. The comparison between (a) and (b) illustrates how the external field pulls the electron charge density in the direction opposite to the field. In both cases the calculations were performed using GAMESS [36] with a triple-zeta valence basis set and added diffuse orbitals.

distribution is suppressed. Including the Stark shift in the exponent, that is using Eq. (12), together with the field-free HOMO (15) clearly increases $\partial^2 P / \partial q_x \partial q_y$ for $q_y > 0$ compared to the standard MO SFA results, but not nearly enough to reproduce the experimental findings [see Fig. 2(b)]. The argument of the exponential in Eq. (12) favors ionization when the electric field has a negative z component, since the Stark-shift-corrected ionization potential is smaller in that case. However, this effect is not enough to overcome the geometrical effect caused by the non-Stark-shifted pre-exponent, containing the field-free HOMO. Hence, we cannot neglect the modification of the initial orbital by the external field. At the peak electric field of the experiment, the contribution of the polarizability term in Eq. (2) is much larger than the contribution of the permanent dipole terms and it is the polarizability response that modifies the initial orbital. Accordingly, the HOMO charge distribution follows the (quasi)static field during the interaction with the circularly polarized field [see Fig. 3(b)]. An approach where one calculates the asymptotic coefficients of the HOMO for each field orientation, to be used in an SFA calculation, becomes impractical since in the saddle-point formulation of

the SFA one would need the coefficients C_{lm} at complex fields (complex times).

Another way to consider the modification of the HOMO in the static picture could be performed by following the approach presented in Ref. [38], suitably modified to describe polar systems. We start from the time-independent Schrödinger equation for an n -electron system, satisfied by the (quasi-stationary) wave function Ψ_n ,

$$E^M(\mathbf{F})\Psi_n = \left(\sum_{j=1}^n (H_j + \mathbf{r}_j \cdot \mathbf{F}) + V_{ee}^n \right) \Psi_n, \quad (16)$$

where $H_j = -(1/2)\nabla_j^2 - \sum_{i=1}^k Z_i/|\mathbf{R}_i - \mathbf{r}_j|$ (Z_i are charges and \mathbf{R}_i are the coordinates of the k nuclei, and \mathbf{r}_j are the electron coordinates), and $V_{ee}^n = \sum_{l < j}^n 1/|\mathbf{r}_l - \mathbf{r}_j|$ contains the electron-electron interaction. We have already included the Stark shift of the total energy of the molecule in $E^M(\mathbf{F})$ in Eq. (16). As in Ref. [38], a Born-Oppenheimer-like ansatz is employed, to decouple the motions of the residual, fast electrons of the ion (coordinates $\mathbf{r}_1, \dots, \mathbf{r}_{n-1}$) and the slow electron that tunnels out (coordinate \mathbf{r}_n). The total wave function is decoupled as

$$\Psi_n(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}, \mathbf{r}_n) = \Psi_{n-1}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}; \mathbf{r}_n) \otimes \Psi_t(\mathbf{r}_n), \quad (17)$$

where the coordinate \mathbf{r}_n is the adiabatic parameter in $\Psi_{n-1}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}; \mathbf{r}_n)$. This ansatz is valid for general complex systems so it can be applied to polar molecules as well. Since it is assumed that $r_n = |\mathbf{r}_n|$ is large, the overlap integrals between the bound electrons and the tunneled electron become negligible so that the antisymmetrization between the $n-1$ core electrons and tunneled electron can be neglected. In the region of large r_n , the electron-electron interaction V_{ee}^n can be approximated retaining only monopole and dipole terms, that is,

$$V_{ee}^n \approx V_{ee}^{n-1} + \frac{(n-1)}{r_n} + \sum_{j=1}^{n-1} \mathbf{r}_j \cdot \mathbf{d}, \quad (18)$$

where $\mathbf{d} = \mathbf{r}_n/r_n^3$ can be thought of as an effective field felt by the residual $n-1$ electrons from the action of the outgoing tunneled electron. The interaction between the nuclei and the slow electron can also be approximated as

$$\sum_{i=1}^k \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_n|} \approx \frac{\sum_{i=1}^k Z_i}{r_n} + \frac{(\sum_{i=1}^k Z_i \mathbf{R}_i) \cdot \mathbf{r}_n}{r_n^3}. \quad (19)$$

The decoupling of (16) leads to the following equation for the bound electron part:

$$E^I(\mathbf{F} + \mathbf{d})\Psi_{n-1} = \left[\sum_{j=1}^{n-1} [H_j + \mathbf{r}_j \cdot (\mathbf{F} + \mathbf{d})] + V_{ee}^{n-1} \right] \Psi_{n-1}, \quad (20)$$

and the tunneled electron part,

$$(E^M(\mathbf{F}) - E^I(\mathbf{F} + \mathbf{d}))\Psi_t = \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r_n} - \frac{(\sum_{i=1}^k Z_i \mathbf{R}_i) \cdot \mathbf{r}_n}{r_n^3} + \mathbf{r}_n \cdot \mathbf{F} \right) \Psi_t, \quad (21)$$

where ∇ operates on the coordinate \mathbf{r}_n and $Z = m - n + 1$ is the charge of the parent ion ($m = \sum_{i=1}^k Z_i$ is the total charge of the nuclei). The left-hand side of Eq. (21) is explicitly given by

$$E^M(\mathbf{F}) - E^I(\mathbf{F} + \mathbf{d}) = -I_p(\mathbf{F}) + (\boldsymbol{\mu}^I + \boldsymbol{\mu}_{\text{ind}}^I) \cdot \mathbf{d} + \frac{1}{2} \mathbf{d}^T \boldsymbol{\alpha}^I \mathbf{d}, \quad (22)$$

where $I_p(\mathbf{F})$ is given by Eq. (2), $\boldsymbol{\mu}_{\text{ind}}^I$ is the induced dipole moment given by

$$\boldsymbol{\mu}_{\text{ind}}^I = \boldsymbol{\alpha}^I \mathbf{F}, \quad (23)$$

and

$$\frac{1}{2} \mathbf{d}^T \boldsymbol{\alpha}^I \mathbf{d} = \frac{1}{r_n^6} (\alpha_{xx}^I x_n^2 + \alpha_{yy}^I y_n^2 + \alpha_{zz}^I z_n^2) \quad (24)$$

is proportional to $1/r_n^4$ at large distances. In the previous equation, α_{xx}^I , α_{yy}^I , and α_{zz}^I are the polarizabilities of the cation along its molecular axes. Equation (21) for the tunneled electron part can be rewritten as

$$-I_p(\mathbf{F})\Psi_t = \left[-\frac{1}{2} \nabla^2 + V_{ef}(\mathbf{r}_n; \mathbf{F}) + \mathbf{r}_n \cdot \mathbf{F} \right] \Psi_t, \quad (25)$$

where

$$V_{ef}(\mathbf{r}_n; \mathbf{F}) = -\frac{Z}{r_n} - \frac{(\boldsymbol{\mu}_T^I + \boldsymbol{\mu}_{\text{ind}}^I) \cdot \mathbf{r}_n}{r_n^3} - \frac{1}{2} \mathbf{d}^T \boldsymbol{\alpha}^I \mathbf{d}, \quad (26)$$

is the *effective* single-active-electron potential viewed from the side of the tunneled electron at large distances. In the previous equation,

$$\boldsymbol{\mu}_T^I = \boldsymbol{\mu}^I + \frac{(\sum_{i=1}^k Z_i \mathbf{R}_i) \cdot \mathbf{r}_n}{r_n^3} \quad (27)$$

is the total permanent dipole of the unrelaxed cation, containing contributions from the nuclear charge in addition to the electronic part of the permanent dipole moment $\boldsymbol{\mu}^I$. The term $(1/2)\mathbf{d}^T \boldsymbol{\alpha}^I \mathbf{d}$ models the polarization of the residual electrons in response to the slow electron.

With the help of the previous potential we can estimate the modification of the HOMO at large distances, exactly as required in a length gauge formulation of the SFA. We can imagine that the quasibound field-modified HOMO $\phi_n(\mathbf{r}_n; \mathbf{F})$ at large r_n satisfies the following equation:

$$-I_p(\mathbf{F})\phi_n(\mathbf{r}_n; \mathbf{F}) = \left(-\frac{1}{2} \nabla^2 + V_{ef}(\mathbf{r}_n; \mathbf{F}) \right) \phi_n(\mathbf{r}_n; \mathbf{F}). \quad (28)$$

At large distances, $(1/2)\mathbf{d}^T \boldsymbol{\alpha}^I \mathbf{d}$ could be neglected, obtaining

$$V_{ef}(\mathbf{r}_n; \mathbf{F}) \approx -\frac{Z}{r_n} - \frac{(\boldsymbol{\mu}_T^I + \boldsymbol{\mu}_{\text{ind}}^I) \cdot \mathbf{r}_n}{r_n^3}. \quad (29)$$

The previous equation provides a clear and intuitive picture of the modification of the effective potential felt by the tunneled electron at large distances. The tunneled electron feels the Coulomb field of the ion and the permanent and induced dipoles of the ion. The field enters the effective potential through the induced dipole part of the potential that appears because of the polarizability of the electronic cloud of the residual electrons [see Eq. (23)]. We note that this is, in fact, a multielectron effect, modeling the polarization of the core electrons due to the electric field. The form of the effective potential, where the field explicitly enters suggests that the

asymptotic properties of the HOMO may be modified by the field. Below we consider this possibility.

The permanent dipole moment and the induced dipole moment appear on the same footing in the effective potential (29). If the considered molecular system is such that the permanent dipole moment of the ion is dominant with respect to the induced dipole, the latter can be neglected. In this case the V_{ef} loses the explicit dependence on the field.

However, for the molecules considered here the polarizability is so large that $\boldsymbol{\mu}_{\text{ind}}^I$ can be larger than $\boldsymbol{\mu}_T^I$, resulting in a substantial modification of the HOMO at tunneling. For example, the induced dipole of the ion of OCS is about three times larger than the permanent dipole of the ion, and this ratio is even larger for the case of benzonitrile (see supplementary information to Ref. [3]). When considering different field directions with respect to the molecular axis, away from the direction specified by the permanent dipole moment of the molecule, $\boldsymbol{\mu}_T^I \cdot \mathbf{r}_n \ll \boldsymbol{\mu}_{\text{ind}}^I \cdot \mathbf{r}_n$. These considerations motivate our scheme to account for the modification of the orbital by the field and neglect $\boldsymbol{\mu}_T^I$ with respect to $\boldsymbol{\mu}_{\text{ind}}^I$ in the effective potential (29), that is,

$$V_{ef}(\mathbf{r}_n; \mathbf{F}) \approx -\frac{Z}{r_n} - \frac{\boldsymbol{\mu}_{\text{ind}}^I \cdot \mathbf{r}_n}{r_n^3}. \quad (30)$$

Since the induced dipole of the ion $\boldsymbol{\mu}_{\text{ind}}^I$ is connected to the electric field vector through the polarizability tensor $\boldsymbol{\alpha}^I$ [see Eq. (23)], it is clear that the instantaneous field orientation *defines* the orientation dependence of the effective potential.

To further assess the modification of the HOMO orbital due to the action of the polarizability response of the inner electrons, it is helpful to consider whether, in a single-active electron picture, the electron emission occurs below or over the barrier. This analysis should be carried out including the static Stark shifts of the neutral and its corresponding cation. Well below the barrier, the coordinate of the turning point of the single-active electron molecular potential plus the field interaction is large, so the Coulomb part of the potential, Z/r_n is much larger than the part of the potential involving the permanent and induced dipole of the cation. Then, the asymptotic properties of the HOMO are given by Eq. (15) and depend exclusively on the field-free C_{lm} coefficients.

If, on the other hand, the field strength is such that ionization occurs over the barrier of the single-active-electron potential such as the case of OCS at the considered experimental intensities [3], the properties of the HOMO should be described at these distances, and not at very large r_n . This is so because classically, the over-the-barrier ionization occurs at the saddle point of the potential formed by the single-active-electron potential and the electron field interaction. For the case of OCS, the saddle point of the potential occurs for distances from 4 to 6 a.u.. At these intermediate distances, both the Coulomb and the dipole part of the effective potentials (29) and (30) are significant so they both have to be taken into account. We note that the action of the induced dipole term is to increase the tunneling barrier; however, at the intensities considered here even with this correction the ionization would occur over the barrier. In addition, at intermediate distances, the HOMO cannot be written in the form (15). The Hamiltonian of (28) is not valid in the inner region near the origin, where the

correlation between all n electrons becomes significant. The outer electron is quasibound even in the inner region (over-the-barrier ionization) and the inner (fast) $n - 1$ electrons respond instantaneously to the field direction. This suggests that the static field would modify the potential in the inner region in a similar manner as in the outer region. Taking the main multielectron effect in the inner region to be the change in the quasistatic Coulomb field experienced by each of the electrons due to the polarization of the multielectron cloud [39], it can be verified that the modifications of the wave function of the tunneled electron, in the field frame, would be independent on the orientation of the field with respect to the molecular axis. Since both in the inner and outer region, the modification of the orbital is similar, and independent of orientation of the field in the molecular frame, one can reach the following conclusions. In cases when the effective potential is of the form (30), the field defines the dominant direction and the form of the field-dressed HOMO at intermediate distances, in the field frame, is independent of the orientation of the field with respect to the molecular axis. On the other hand, when the permanent dipole of the cation cannot be neglected with respect to the induced dipole [i.e., when the form of the effective potential is given by (29)], both the field direction and the direction of the permanent dipole moment of the cation are present, therefore, the form of the field-dressed HOMO at intermediate distances would be different for different orientations of the field with respect to the permanent dipole of the cation. In other words, the orbital would again be modified, but, in general, the modifications would be different for different field orientations. The modifications of the initial orbital in the over-the-barrier ionization regime comes as no surprise, since a similar conclusion has been reached in the barrier-suppression regime for atoms [40].

D. Simplified model and comparison with the experiment

OCS and benzonitrile considered here belong to the class of systems with very large polarizability and their strong-field ionization takes place in the over-the-barrier ionization regime. From the previous discussion, the properties of the field-distorted HOMO are approximately independent of the orientation of the field with respect to the molecular axis. To model the insensitivity of the modification of HOMO with respect to the field orientation, it is possible to simplify the situation by replacing the HOMO with a model orbital for which the C_{lm} coefficients are independent of the orientation of the field with respect to the molecular axis. The s orbitals have this property and can therefore be used to account for the modification of the HOMO in the field when polarizabilities are substantial in the sense discussed and established in the previous paragraphs. Therefore, it seems reasonable to model the initial HOMO by an s orbital, retaining the Stark-shift correction of the ionization potential (2). The same approach was applied when introducing Stark-shift corrections into the tunneling model (see supplementary information to Ref. [3]). Therefore, in the case of OCS the Stark-shift-corrected SFA of Eq. (12) is used where ϕ_n is a simple atomic $1s$ orbital. Figure 4 shows the result of such a calculation, the parameters of the laser field being the same as in Fig. 2. Indeed, the calculated momentum distributions show asymmetry in the correct direction and compare very well to the momentum

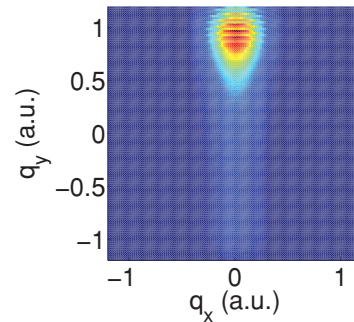


FIG. 4. (Color online) Stark-shift-corrected photoelectron momentum distributions, $\partial^2 P / \partial q_x \partial q_y = \int (\partial^3 P / \partial q_x \partial q_y \partial q_z) dq_z$, for the ionization of an artificial OCS molecule, one-dimensionally oriented such that the O end points in the positive z direction, where the initial orbital entering Eq. (12) is modeled by a simple s orbital. The laser parameters and the color scale are the same as in Fig. 2.

distributions obtained in the Stark-shift-corrected tunneling model, depicted in Fig. 3(a) in Ref. [3]. This agreement stems from the general agreement of tunneling with the SFA in the adiabatic limit [31].

In the case of strong-field ionization of oriented C_7H_5N , exploiting the polarization anisotropy of the molecule, an experimental three-dimensional (3D) orientation of the molecule was achieved [3]. The 3D orientation is such that the CN end points in the positive z direction while the benzene ring is fixed in the (y,z) plane. For such an orientation, the polarization plane of the circularly polarized laser field lies entirely in the nodal plane of the initial HOMO. Then an *ad hoc* correction to the tunneling model is performed to theoretically reproduce the experiment (see supplementary information to Ref. [3]). For the SFA no such correction is necessary, since nodal plane structures are automatically taken into account [29,30]. Apart from the preservation of the nodal plane, the structure of the HOMO of C_7H_5N off the nodal plane is modified by the field (polarizability terms are even more important than in the case of OCS), hence, as in the case of OCS, it is inaccurate to use the field-free HOMO as the initial state. In this case, the same argument for the modification of molecular orbitals as in the OCS case holds. The difference here is the existence of the nodal plane (i.e., the model orbital must have a nodal plane where the original orbital has one). Since the field here rotates in the nodal plane of the orbital, because of symmetry reasons no strong-field modification of the orbital due to polarizability can wash out the nodal plane. Away from the nodal plane, the extreme polarizability would again result in insensitivity of the form of the laser-dressed HOMO, in the field frame, to the field orientation with respect to the molecular axis. This motivates modeling of the field-modified orbital by the simplest orbital possessing a nodal (y,z) plane for which asymptotic properties are insensitive to the field direction—the p_x orbital. Using Eq. (12), with an initial p_x orbital, as in the tunneling model [3], the photoelectron momentum distribution of Fig. 5 is obtained. The nodal plane of C_7H_5N is clearly seen in the distribution and we observe very good agreement with the tunneling calculations on C_7H_5N presented in Fig. 3(c) in Ref. [3].

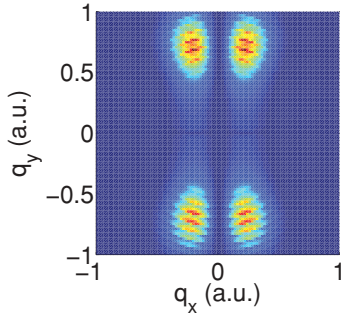


FIG. 5. (Color online) Stark-shift-corrected photoelectron momentum distributions, $\partial^2 P / \partial q_x \partial q_y = \int (\partial^3 P / \partial q_x \partial q_y \partial q_z) dq_z$, for the ionization of an artificial C_7H_5N molecule, three-dimensionally oriented such that the N end points in the positive z direction while the benzene ring is fixed in the (y, z) plane, where the initial orbital entering Eq. (12) is modeled by a simple p_x orbital. The laser intensity is $I = 1.2 \times 10^{14}$ W/cm². The other laser parameters and the color scale are the same as in Fig. 2.

V. CONCLUSION

We have shown that in order to describe strong-field ionization of molecules with large permanent dipole moments and polarizabilities, it is necessary to account for the modification of the ionization potential due to the Stark shifts. The systematic inclusion of the Stark shifts in the MO SFA presented here enables correction of the model in the tunneling limit. On top of that, we have shown that it is necessary to consider dynamic modifications of the molecular orbitals in intense laser fields, especially in the case of large polarizabilities. In cases of extreme modification of the initial orbital, simple, atomic-like orbitals could be used as a model for the initial molecular orbital. The results obtained from this simple modification of the MO SFA compare very well with the experimental results, capture the essential physics, and account for the existence of the nodal planes of the initial molecular orbitals.

While our work shows the power of the simple models, especially the simple models for the initial HOMO in the presence of external fields, it also highlights the need for more advanced theoretical modeling to include the dynamic modifications of the molecular orbital caused by the strong laser field. One possible extension of the present model for the

modification of molecular orbitals by slowly varying strong fields might be numerical calculation of the field-modified HOMO using the potential (29) in the outer region and a field-modified single-active-electron potential for the inner region, using the imaginary time propagation on a grid.

It is also clear that the accuracy of the present approach will be system dependent for another reason. The present theory (as any other that uses the Volkov state as a final state) neglects the molecular potential in the final state. Hence, asymmetries in the spectra induced by the leading asymmetric dipole term of the molecular potential are not accounted for. If, as is the case for OCS and benzonitrile considered here, the transition into the continuum occurs at points in space that are well separated from the center of mass, the neglect of this dipole is accurate. In other systems this asymmetry would have to be accounted for [e.g., by including the dipole potential into the quantum trajectory approach discussed in Ref. [41].

APPENDIX

The transition amplitude of Eq. (12) is evaluated as follows. Ionization primarily occurs at large distances from the core and, hence, it is accurate to use the asymptotic form of the initial state, given by Eq. (15), in the evaluation of the spatial integral in Eq. (12). Furthermore, we use the saddle-point approximation to evaluate the spatial integral, obtaining

$$T_{fi} = \sum_{t_s} f(t_s) \sqrt{\frac{2\pi i}{S''(t_s)}} \exp[iS(t_s)], \quad (31)$$

where $S(t) = (1/2) \int_0^t (\mathbf{q} + \mathbf{A})^2 dt' + \int_0^t I_p(\mathbf{F}) dt$ is the Stark-shift-corrected semiclassical action, and t_s are the saddle points, obtained from $S'(t_s) = 0$. Provided that we neglect the Stark shift in the preexponent,

$$f(t_s) \propto \sum_{lm} C_{lm} Y_{lm}(\hat{\mathbf{Q}}(t_s)) \left(\frac{Q(t_s)}{i\kappa} \right)^l \frac{\Gamma(l + \nu + 2)}{2^l \Gamma(l + 3/2)} \times {}_2F_1 \left(\frac{l - \nu}{2}, \frac{l - \nu + 1}{2}, l + \frac{3}{2}, -\frac{Q^2(t_s)}{2I_p(0)} \right) \frac{1}{S'_0(t_s)^\nu}, \quad (32)$$

where $\mathbf{Q} = \mathbf{q} + \mathbf{A}$, $\nu = Z / \sqrt{2I_p(0)}$, Z is the ionic charge, and $S_0(t) = (1/2) \int_0^t (\mathbf{q} + \mathbf{A})^2 dt' + I_p(0)t$.

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