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# The influence of permanent dipole and dynamic core-electron polarization on tunneling ionization of polar molecules

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We present detailed theoretical investigation on strong-field ionization of polar (CO and NO) as well as non-polar molecules (N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>). Our results indicate that the account for the Stark correction in the molecular tunneling ionization theory leads to overall fairly good agreements with numerical solutions of the time-dependent Schrödinger equation (TDSE). Furthermore, we show that the effect of dynamic core-electron polarization, in general, has a weak influence on the angle-dependent ionization probability. However, in case of CO we confirm the recent finding by Zhang *et al.* [Phys. Rev. Lett. **111**, 163001 (2013)] that the account for dynamic core-polarization is crucial to achieve an overall good agreement with experiments.

## I. INTRODUCTION

Over the last three decades interest in strong-field ionization has been significantly increased. In fact, it has been found that all the important strong-field phenomena, which involve rescattering physics, starts with ionization step [1]. New imaging techniques based on rescattering such as laser-induced electron diffraction [2, 3] and high-order harmonics spectroscopy [4–7] are now capable of probing dynamic molecular structural changes with unprecedented sub-Ångstrom spatial and few-femtosecond temporal resolutions. Correct interpretation and extraction of target structures depend critically on accurate description of the ionization step. Furthermore, high-order harmonics generation (HHG) is now routinely used as tabletop broadband coherent light sources in the extreme-ultraviolet (XUV) to soft X-ray regions with pulses as short as tens of attoseconds [8–11]. These new light sources are currently limited by their low conversion efficiency. One of the possible methods to enhance HHG yields is the waveform synthesis, which relies on the precise control of the ionization step [12].

Despite its importance, the description for angle-dependent ionization from molecules is still semi-quantitative at best. In fact, ionization from atomic targets has been quite well understood based on Perelomov, Popov and Terentev (PPT) [13] theory or its quasi-static tunneling limit, the so-called Ammosov-Delone-Krainov (ADK) theory [14]. The extension to molecules, the so-called MO-ADK [15] and MO-PPT [16, 17] have been found to work reasonably well for diatomic homonuclear molecules, such as H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> [18, 19]. These results lead to a general belief that ionization yields reflect the shape of the highest occupied molecular orbital (HOMO), as one would expect based on the intuitive picture within the MO-ADK theory. With the ability to align molecules [20] tunneling ionization has therefore been proposed as

a possible method for direct imaging of the geometry of the ionizing orbital [18, 19, 21]. The situation is not quite clear for polar molecules. It was found in Ref. [22] that the Stark shift had to be taken into account in a modified MO-ADK theory in order to reproduce the experimental data for OCS. However the measurements for CO molecule [23–25] showed that the Stark-corrected MO-ADK (or SC-MOADK) disagrees strongly with experiments. On the contrary to the OCS case, these results imply that the Stark effect should play a minor role in tunneling ionization from CO. The recently developed weak field asymptotic theory (WFAT) [26, 27] also disagrees with the experiments for CO and agrees with the SC-MOADK theory. The agreement between the WFAT and SC-MOADK is expected since the SC-MOADK theory can be approximately reduced to the WFAT. Note that the more involved strong-field approximation (SFA) [28] can also be extended to polar molecules [23, 29]. However, the standard SFA generally suffers from the gauge-dependence problem [30] and the results are origin dependent [31, 32]. The WFAT (and therefore, the SC-MOADK) are formally origin-independent [26]. In this paper we therefore only focus on the MO-ADK and its modifications.

Quite recently, Zhang *et al* [33] showed that experimental data for CO in Refs. [23, 25] can be nicely reproduced if dynamic polarization of the core electrons is taken into account. The importance of the multi-electron effect, in particular, the influence of core polarization, was also reported for static field ionization in Refs. [34, 35]. Note that the effect of the dynamic core polarization was considered earlier in the context of photoelectron momentum distribution [36]. It was also found that the account for this effect is important for the correct reading of the attoclock experiments by Pfeiffer *et al.* [37], even for argon. Furthermore, this effect has been shown to be responsible for the presence of the low-energy photoelectrons observed in the experiments for naphthalene by laser pulses

with large ellipticity [38].

How reliable are the Stark-corrected MO-ADK or the WFAT theories for polar molecules? And, how significant is the dynamic core polarization effect for other molecules, besides CO, for ionization in typical intense infrared or mid-infrared lasers? These questions have not been addressed in details in all the above studies. The goal of this paper is two-fold. First, we show that the account for the Stark correction in polar molecules leads to an overall improvement over the standard MO-ADK theory. However, the current theories overestimate this effect, except for the case of small permanent dipoles. Second, we show that the dynamic core polarization indeed has a strong effect on the angle dependent ionization from CO, but not much for other targets considered in this paper.

The rest of this paper is organized as follows. In Sec. II we describe theoretical methods used in our paper. In Sec. II.A we describe our method for numerical solution of the time-dependent Schrödinger equation (TDSE) for an active electron in a few-cycle strong laser pulse, with and without the account for the dynamic core-polarization. The Stark-corrected MOADK theory and its relation to WFAT will be briefly described in Sec. II.B. Our results will be presented in Sec. III for the so-called  $Z_1Z_2$  model (in Sec. III.A), polar molecules CO and NO (in Sec. III.B and III.C), as well as non-polar molecules  $N_2$ ,  $O_2$ , and  $CO_2$  (in Sec. III.D). Finally, we finish our paper with a summary. Atomic units are used throughout the paper, unless otherwise indicated.

## II. THEORETICAL METHODS

### A. Numerical solution of the time-dependent Schrödinger equation and ionization probability

We treat a target linear molecule within the single-active-electron (SAE) approximation. The Hamiltonian for such a target in the presence of a linearly polarized laser pulse can be written as

$$\hat{H} = \hat{H}_0 + V_L(\mathbf{r}, t) + V_p(\mathbf{r}, t), \quad (1)$$

with the field-free Hamiltonian as

$$\hat{H}_0 = -\frac{\nabla^2}{2} + V_0(\mathbf{r}). \quad (2)$$

The SAE model potential  $V_0(\mathbf{r})$  is constructed using the approach that has been used previously in Refs. [39, 40]. This potential consists of electrostatic and exchange-correlation potentials. In our paper, we evaluate the exchange within the local density approximation (LDA). To have a correct Coulombic asymptotic behavior, we follow the so-called  $LB\alpha$  model [41] and further add a gradient correction term, for details see Refs. [39–41]. The model potentials are constructed by using the Gaussian quantum chemistry package [42], which typically are not quite

accurate at large distances due to the basis sets based on the Gaussian-type orbitals. We therefore smoothly replace the potential at the asymptotic distances by  $-1/r$  potential, typically for  $r > 10$  a.u.

In Eq. (1), the electron-laser interaction is

$$V_L(\mathbf{r}, t) = \mathbf{E}(t) \cdot \mathbf{r}, \quad (3)$$

where  $E(t)$  is the time-dependent laser electric field amplitude. Following Ref. [33] we also take into account the interaction of the active electron with the dynamic polarization of core electrons induced by the laser. This potential is written as

$$V_p(\mathbf{r}, t) = -\frac{\mathbf{E}(t)\hat{\alpha}_c\mathbf{r}}{r^3}, \quad (4)$$

where  $\hat{\alpha}_c$  is the total polarizability tensor due to core electrons (see Table I and discussion below). Note that the same approach has also been used before by Shvetsov-Shilovski *et al.* [36] and Pfeiffer *et al.* [37] for the treatment of photoelectron momentum distribution. Within the SAE approximation, the total dipole polarizability due to the core electrons is taken to be of the cation, as in Refs. [36, 37]. To avoid the singularity at  $r = 0$  we follow Zhang *et al.* [33] and apply a cutoff for  $V_p$  in Eq. (4) at certain  $\mathbf{r}_c$ . The cutoff  $\mathbf{r}_c$  can be defined as an ellipsoidal surface where potentials due to polarization field and laser field cancel each other. We have found that the TDSE results are rather insensitive to small changes in the position of  $\mathbf{r}_c$ . We remark that in all calculations the nuclei are fixed at the experimental equilibrium positions.

The laser is linearly polarized in the  $yz$  plane with an angle  $\beta$  between the electric field at the peak of the pulse and the molecular axis (taken to be along the  $z$ -axis). The electric field is taken to have the form  $E(t) = E_0 \sin^2(\frac{\pi t}{\tau}) \sin(\omega t + \phi)$ . Here,  $E_0$  is the peak field amplitude;  $\omega$  is the laser carrier frequency;  $\phi$  is the carrier-envelope phase chosen to be  $\pi/2$  in our calculation;  $\tau$  is the pulse duration equal to three cycles in the case of CO molecule and two cycles for the other cases. A typical laser pulse is shown in Fig. 1(a) for the case of a two-cycle pulse. Note that in the tunneling regime, it is expected that ionization occurs predominantly near the peak of the pulse when the laser points towards the positive  $z$ -direction if  $\beta \leq 90^\circ$ , or towards the negative  $z$ -direction if  $\beta \geq 90^\circ$ . This choice of short pulses is made for easy comparison with the earlier calculations in Refs. [33, 43].

The TDSE with Hamiltonian (1) is solved by second-order split operator method [5]. Briefly, the wavefunction at time  $t + \Delta t$  is calculated from a previous time step  $t$  by

$$\begin{aligned} \psi(\mathbf{r}, t + \Delta t) &= e^{-i\hat{H}\Delta t}\psi(\mathbf{r}, t) \\ &\approx e^{-\frac{i\hat{H}_0\Delta t}{2}} e^{-iV\Delta t} e^{-\frac{i\hat{H}_0\Delta t}{2}} \psi(\mathbf{r}, t) \end{aligned} \quad (5)$$

This propagation starts from the initial wavefunction at time  $t_i = t_0$ , normally the ground state of the target, and finishes when the laser pulse is over at  $t_f$ .

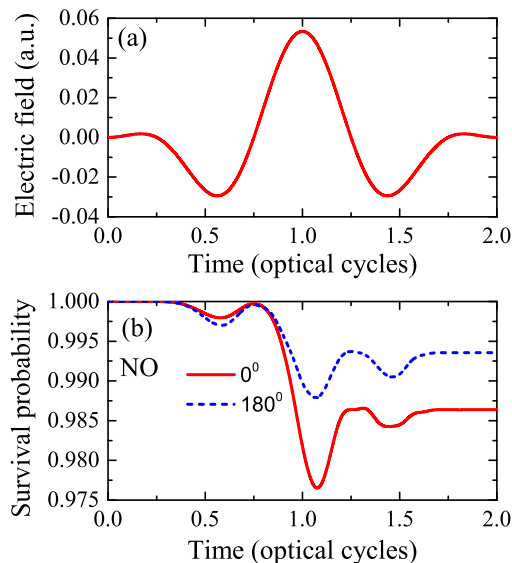


FIG. 1. (Color online) (a) A typical two-cycle laser pulse with an wavelength of 800 nm and an intensity of  $10^{14}$  W/cm<sup>2</sup> used in the TDSE calculations. (b) Typical survival probability of the ground state (HOMO) of NO oriented at  $\beta = 0^\circ$  and  $180^\circ$  under the laser pulse shown in (a).

The ionization probability is given by

$$P(t) = 1 - \sum_n |\langle \psi(\mathbf{r}, t) | \Psi_n(\mathbf{r}) \rangle|^2, \quad (6)$$

for  $t = t_f$ , where  $\Psi_n(\mathbf{r})$  being the bound state wavefunctions. To ensure the convergence, we also propagate further after the laser field is turn-off so that all ionization flux reaches to the absorbing boundary. We use a spherical box with a radius of 80 a.u. with 400 radial grid points. To avoid artificial reflection due to a finite box size, we use a mask function as described in Ref. [5]. We also used 31 partial waves and a time-step of 0.03 a.u. in our calculations. These parameters have been carefully checked to make sure the convergence was reached to within a few percent error. Note that at each time step during the time propagation we have restricted the active electron from the orbitals occupied by the core electrons [44].

Molecule	$\alpha_{cxx} = \alpha_{cyy}$	$\alpha_{czz}$
CO	6.72	12.22
NO	6.12	10.75
N <sub>2</sub>	2.84	9.48
O <sub>2</sub>	5.41	9.33
CO <sub>2</sub>	9.95	24.06

TABLE I. The non-zero components of total polarizability tensor (in a.u.) due to core electrons for a few molecules.

To model polarizability of core electrons, we used Gaussian 03 quantum chemistry package [42]. The polarizability can also be obtained by fitting the total energy

of the target cation in weak electric fields to the quadratic polynomials in electric field strength. The two methods gave virtually identical results. We show in Table I the non-zero values of dipole polarizabilities due to core electrons for CO, NO, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>.

We remark that due to the nature of the SAE approximation used in our calculations, our model parameters are different from the single active orbital model used by Zhang *et al* [33]. In particular, in case of CO molecule, their core-electron polarizability (due to  $1\pi$  and  $4\sigma$  electrons) is somewhat smaller. In fact, in Zhang *et al* all  $5\sigma$  electrons are active and both direct and exchange interactions with core electrons are calculated at each time step, although the core electrons are frozen. Our approach is simpler and has been used in Refs. [36, 37, 39, 40, 44]. Our approach would likely overestimate the core polarization at small  $r$ . Nevertheless, we will show below that our numerical results using the SAE picture are in good agreement with their data and with experiments [25]. As an illustration, we show in Fig. 1(b) the survival probability [i.e.,  $1 - P(t)$ ] for NO molecule aligned at  $0^\circ$  and  $180^\circ$  for the laser parameters indicated in the caption.

## B. Approximate theories on strong-field ionization for polar molecules

The Stark-corrected MOADK (SC-MOADK) theory is an approach based on the heuristic extension of the standard MO-ADK theory [15], in which the Stark-shifted ionization potential is used instead of field-free ionization potential  $I_p(0) \equiv I_p$  [22, 23], as

$$I_p(\mathbf{E}) = I_p(0) + \Delta\boldsymbol{\mu}\mathbf{E} + \frac{1}{2}\mathbf{E}^T\Delta\hat{\boldsymbol{\alpha}}\mathbf{E} + \dots \quad (7)$$

Here  $\Delta\boldsymbol{\mu}$  (or  $\Delta\hat{\boldsymbol{\alpha}}$ ) is the difference between the dipoles (or dipole polarizability tensors) of the neutral molecule and its cation. Within the SAE approximation, the dipole and dipole polarizabilities of the active electron ground state (HOMO) are used.

The WFAT has been developed recently for quasi-static treatment of tunneling ionization [26, 27]. Its main difference from the MO-ADK is the presence of a new factor  $\exp(-2\kappa_0\mu_z)$  where  $\kappa_0 = \sqrt{2I_p(0)}$  and  $\mu_z$  is the projection of the permanent dipole of the HOMO on the electric field direction. As such, the WFAT can be used for polar molecules. In case of relatively small Stark shifts, WFAT can be shown to be equivalent to SC-MOADK theory. Indeed, for a small Stark correction  $\mu_z F$  as compared to the field-free ionization potential, we have

$$\begin{aligned} \kappa^3 &= [2(I_p(0) + \mu_z F)]^{3/2} = \kappa_0^3 \left(1 + \frac{2\mu_z F}{\kappa_0^2}\right)^{3/2} \\ &\approx \kappa_0^3 + 3\kappa_0\mu_z F. \end{aligned} \quad (8)$$

Therefore the main exponent factor in SC-MOADK theory can be simplified to

$$\exp\left(\frac{-2\kappa^3}{3F}\right) = \exp\left(\frac{-2\kappa_0^3}{3F} - 2\kappa_0\mu_z\right). \quad (9)$$

We remark that the structure coefficients  $C_{lm}$  in the standard MO-ADK theory [15] depend on the choice of the origin of the single-center expansion. This did not cause any problem for molecules with a center of symmetry, in particular, for homonuclear diatomic molecules considered in the original paper by Tong *et al* [15]. For molecules without a center of symmetry one typically chooses for the origin the center of mass or the center of charge of all nuclei, as in standard quantum chemistry software such as Gaussian [42]. Based on the discussion above, one can also choose the coordinates frame such that the permanent dipole of the HOMO vanishes. In that case, the effect of a permanent dipole on ionization within the MO-ADK theory is solely determined by the “new” structure coefficients in the shifted coordinates system. As shown by Tolstikhin *et al* [26], the WFAT theory is formally invariant under such a translation.

It is important to note that the correction factor in the WFAT depends only on the ionization potential and projection of permanent dipole on the electric field direction, and does *not* depend on the intensity of the field. For our purpose in the following we will mostly compare our TDSE results with SC-MOADK theory. To calculate the ionization probability with a SC-MOADK rate at a fixed orientation angle  $\beta$ , we integrate the probability over the laser pulse under the quasi-static approximation.

In a similar manner to the SC-MOADK theory, the MO-PPT theory [16] can also be extended to include the Stark shifts into the ionization potential, for the treatment of polar molecules. We will call such extension Stark-corrected MO-PPT (or simply SC-MOPPT). As for the PPT theory, we expect SC-MOPPT to have a broader range of applicability in the multiphoton regime, than the quasi-static MO-ADK theory.

### III. RESULTS

#### A. $Z_1Z_2$ model

First we consider the so-called  $Z_1Z_2$  model which consists of two nuclei with charges  $Z_1$ ,  $Z_2$ , and one electron. A similar model was used before in the context of the WFAT [26], for orientation angles  $\beta = 0^\circ$  and  $180^\circ$  between the molecular axis and electric field direction. For our purpose we choose two nuclei with charges  $Z_1 = 0.7$  a.u. and  $Z_2 = 0.3$  a.u. The two nuclei are fixed with at the internuclear distance  $R = 2.0$  a.u. along  $z$ -axis. The origin is chosen to be at the center of charge of the nuclei, with  $Z_1$  at the negative  $z$ -axis.

We solved the time-independent Schrödinger equation for this model by the discrete variable representation method. The ground state (with  $\sigma$  symmetry) energy was found to be 10.5 eV. The MO-ADK structure coefficients  $C_{lm}$  can be found quite accurately by matching the wavefunction at large  $r$  to its asymptotic values [15], see Fig. 2. They were found to be  $C_{00} = 1.6522$ ,  $C_{10} = -0.0841$ ,  $C_{20} = 0.0580$ ,  $C_{30} = 0.0022$ . The coefficients

with  $l > 3$  are very small and contribute little on ionization rate. The permanent dipole due to the electron was found to be 0.19 a.u., pointing to positive  $z$ -axis. This is due to a larger electron density near  $Z_1$  center.

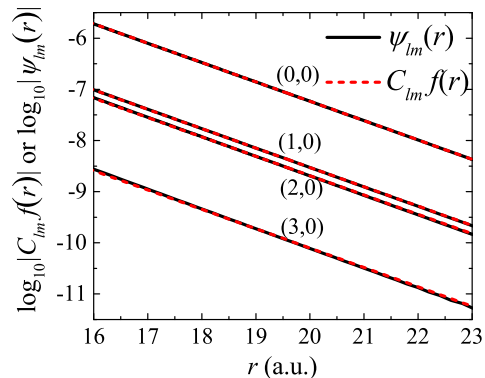


FIG. 2. (Color online) The extraction of the structure coefficients  $C_{lm}$  of  $Z_1Z_2$  model. Indices  $(l, m)$  are indicated in the figure for different  $l$  from 0 to 3.  $f(r) = \exp(-\kappa_0 r)$  is the radial part of the wavefunction at the asymptotic limit.

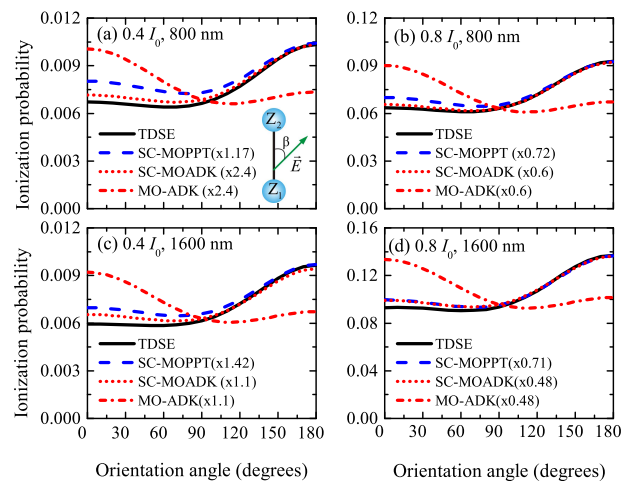


FIG. 3. (Color online) Ionization probabilities vs orientation angle  $\beta$  of  $Z_1Z_2$  molecule under different two-cycle lasers. The laser parameters are indicated in each figure. Results from approximate theories have been normalized to that of the TDSE result at the peaks ionization probability. The normalization factors are given in the labels. Angle  $\beta$  is defined as shown in the inset of (a). Note that  $I_0 = 10^{14}$  W/cm<sup>2</sup> in the label.

For benchmarking with different approximate theories, we carried out TDSE calculations for two laser wavelengths of 800nm and 1600 nm and at two different intensities of  $0.4 \times I_0$  and  $0.8 \times I_0$ , where  $I_0 = 10^{14}$  W/cm<sup>2</sup>. This covers the range of Keldysh parameter  $\gamma$  from 1.48 to 0.524. The laser pulse duration of two cycle was used

in all the cases here. The angle dependent ionization probabilities from the TDSE are compared with different theories in Fig. 3. Note that for easy comparison we have normalized the approximate results to that of the TDSE at the peak values at  $\beta = 180^\circ$ . The normalization factors are given in the labels. Note that the normalization for the ionization rates are still meaningful as the ionization probability is around 10% or smaller in all the cases considered in this paper. In all the cases, the peak ionization probability from the MO-ADK is at  $0^\circ$ . This is expected based on the general MO-ADK intuitive picture as there is a larger electron density near  $Z_1$  center. Clearly, these MO-ADK predictions are in disagreements with the TDSE results.

The account for the Stark shift in the ionization potential brings the SC-MOADK to good agreements with the TDSE in all four cases, although an overall correction factor is needed for each case. The WFAT results (not shown in the figure) are virtually identical to the SC-MOADK results. Similar good agreements are seen for the SC-MOPPT results. The agreement is best for Fig. 3(d) for  $0.8 \times 10^{14}$  W/cm<sup>2</sup> with the wavelength of 1600 nm, in a rather deep tunneling regime with Keldysh parameter  $\gamma = 0.524$ , while it is worse for Fig. 3(a) when  $\gamma = 1.48$ . As discussed in Sec. II.B, the correction factor to the MO-ADK due to the presence of a permanent dipole is proportional to  $\exp(-2\kappa_0\mu \cos\beta)$ . This factor is 0.72 and 1.4 at  $\beta = 0^\circ$  and  $180^\circ$ , respectively. For a target with such a weak asymmetry in ionization, this small correction factor reverses the peak ionization probability as observed all cases shown in Fig. 3. Our results in this subsection clearly illustrate the importance of Stark correction for accurate description of ionization within the MO-ADK approach. For completeness, we remark that the second order correction to Stark shift is very small and practically has no significant effect on the SC-MOADK results.

## B. Tunneling ionization from CO

The TDSE results for ionization probability from CO with 800 nm laser with an intensity of  $2 \times 10^{14}$  W/cm<sup>2</sup> and with 1600 nm laser with an intensity of  $10^{14}$  W/cm<sup>2</sup> are shown in Fig. 4(a) and 4(c), respectively. In both cases, a three-cycle pulse was used for easy comparison with Ref. [33]. Our results for 800 nm case is in a good agreement with Zhang *et al* [33] result within their single-active orbital approximation, in which the ionization peaks at  $\beta = 180^\circ$ , with a rather weak asymmetry. The MO-ADK results, shown in Fig. 4(b) and 4(d), all have a peak at  $0^\circ$  and are qualitatively different from the TDSE results. Again, the MO-ADK results can be understood as the consequences of the larger electron density near the carbon center, which makes it easier for the electron to ionize when electric field is pointed from C to O (that is, along positive  $z$ -direction, or  $\beta = 0^\circ$ ). So the situation here is quite similar to that of  $Z_1Z_2$  model

(see the previous subsection). In both cases the HOMOs are with  $\sigma$  symmetry. Also, similarly to  $Z_1Z_2$  case, the account for the Stark shift reverses the preferential direction of ionization. In fact, the SC-MOADK result is in a qualitative agreement with the TDSE, although the peak at  $\beta = 180^\circ$  is much more pronounced. This indicates that the SC-MOADK overestimates the Stark effect. For the 1600 nm case, the peak in the TDSE ionization probability at  $\beta = 180^\circ$  is more pronounced and the overall agreement with the SC-MOADK is somewhat better, although the Stark effect is still overestimated. For both cases, the SC-MOPPT results are nearly identical to that of the SC-MOADK.

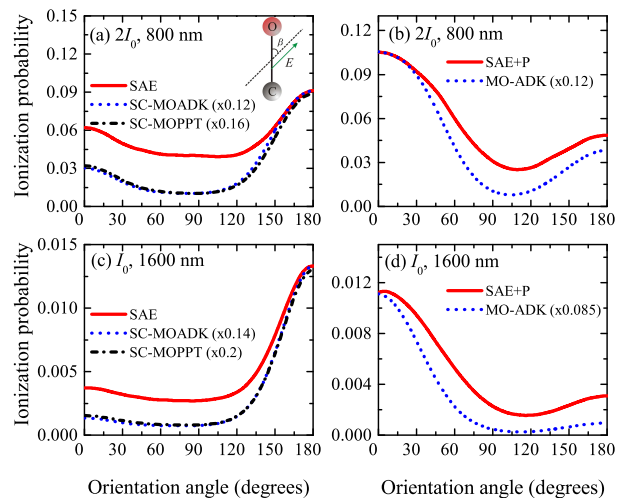


FIG. 4. (Color online) (a) Comparison of the TDSE result (labeled as SAE) with the SC-MOADK and SC-MOPPT for ionization probability of CO with a three-cycle pulse of wavelength of 800 nm and an intensity of  $2 \times 10^{14}$  W/cm<sup>2</sup>. (c) Same as (a) but for the wavelength of 1600 nm and intensity of  $10^{14}$  W/cm<sup>2</sup>. (b) and (d): Same as (a) and (c), respectively, but for the TDSE with dynamic core polarization (labeled as SAE+P) and the MO-ADK. Angle  $\beta$  is defined as shown in the inset of (a). Results from the approximate theories have been normalized to that of the TDSE at the maximal ionization.

Our results above for the MO-ADK and SC-MOADK are in agreement with theoretical results by Li *et al* [23], but in disagreement with their experimental data and the newer measurements by Wu *et al* [25]. In fact, all these experiments indicate that ionization is more preferable near  $\beta = 0^\circ$ . As pointed out by Zhang *et al* [33], the dynamic polarization of core electrons induced by the laser has a very strong effect on the ionization in CO. Indeed, by taking into account the dynamic core polarization in the single active orbital approximation within the time-dependent Hartree-Fock approach, they were able to reproduce the experimental data by Wu *et al* [25]. Our TDSE results with dynamic core polarization [see Eq. (4)] are shown in Fig. 4(b) and 4(d) for 800 nm and 1600 nm

lasers, respectively, are indeed very close to Zhang *et al* [33]. The failure of the SC-MOADK theory to reproduce the experimental data is therefore not surprising, since the SC-MOADK is essentially a SAE model without the core polarization effect. As pointed out by Zhang *et al*, the effect of core polarization is, in general, to reduce the first order Stark shift.

For completeness we remark that all the calculations were done with the nuclei fixed at  $R = 2.13$  a.u. Within our model, the ionization potential and the permanent dipole of the HOMO were found to be 13.4 eV and 1.67 a.u., respectively. The retrieval of the structure coefficients  $C_{lm}$  was performed in a similar fashion as for  $Z_1Z_2$  model. The resulting  $C_{lm}$  were found to be nearly identical to that of Zhao *et al* [40].

Based on the above results, we conclude that the relatively good agreement with experiments for CO by the standard MO-ADK theory should be considered as accidental. Similarly, the relatively good agreement of the SFA calculation in Li *et al* [23] and its modifications in Ref. [43] with experiments should also be classified as accidental. In fact, all these results are based on the SAE approximation and therefore should be compared with the TDSE results shown in Fig. 4(a) and (c). The SFA theory underestimates the Stark correction, whereas the SC-MOADK tends to overestimate this effect.

### C. Tunneling ionization from NO

To further benchmark the SC-MOADK and understand the effect of dynamic core polarization, in this subsection we investigate ionization from NO, a polar molecule with the HOMO in  $\pi$  symmetry. The TDSE results with the wavelength of 800 nm and 1600 nm are shown in Fig. 5(a) and 5(b), respectively, together with the results from approximate theories. An intensity of  $10^{14}$  W/cm<sup>2</sup> was used in both cases. All the results have been normalized to that of the TDSE at the peak ionization near  $\beta = 45^\circ$ .

The MO-ADK results agree fairly well with the TDSE results for both wavelengths. As usual, the MO-ADK rate reflects the electron density of the HOMO of  $\pi$  symmetry. In particular the positions of maxima near  $\beta = 45^\circ$  and  $140^\circ$  and minima near  $\beta = 0^\circ$ ,  $100^\circ$ , and  $180^\circ$  in angle dependent ionization probability are nicely reproduced by the MO-ADK theory, although the peak near  $140^\circ$  is underestimated. The SC-MOADK results show slightly better agreements with the TDSE results for both wavelengths. The agreements deteriorate somewhat at the weaker peak near  $\beta = 140^\circ$ . Again the SC-MOADK theory overestimates the Stark correction, even though the permanent dipole of the HOMO is only 0.28 a.u., see also Ref. [23]. The SC-MOPPT results are virtually identical to that of the SC-MOADK.

As shown in Fig. 5(a) and 5(b), the account for the dynamic core polarization [see Eq. (4)] does not change the TDSE results significantly for both wavelengths. Indeed,

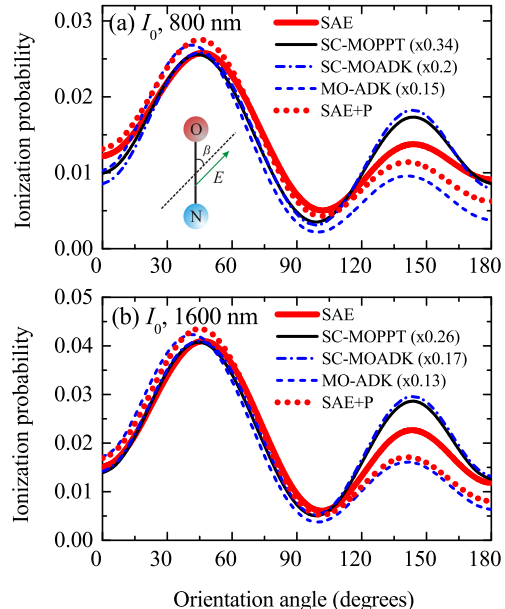


FIG. 5. (Color online) (a): Comparison of the TDSE result (labeled as SAE) with the MO-ADK, SC-MOADK, and SC-MOPPT for ionization probability of NO with a two-cycle pulse of wavelength of 800 nm and an intensity of  $10^{14}$  W/cm<sup>2</sup>. The TDSE result with dynamic core polarization (labeled as SAE+P) is also shown. (b): Same as (a) but for the wavelength of 1600 nm. Angle  $\beta$  is defined as shown in the inset of (a). Results from the approximate theories have been normalized to that of the TDSE (without core polarization) at the maximal ionization.

the shape of ionization probability as a function of orientation angle  $\beta$  remains nearly the same as without the core polarization. The largest change is near  $\beta = 180^\circ$  where it is reduced by about 30%. All these results are in agreements with experiments by Li *et al* [23] and by Endo *et al* [45].

### D. Ionization from non-polar molecules

To further investigate the effect of core polarization on tunneling ionization, we compare the TDSE results with and without the dynamic core polarization [see Eq. (4)] for  $N_2$ ,  $O_2$ , and  $CO_2$  in Fig. 6(a), (b), and (c), respectively. The calculations were done with 800 nm laser with an intensity of  $2 \times 10^{14}$  W/cm<sup>2</sup> for  $N_2$  and  $CO_2$ , and  $10^{14}$  W/cm<sup>2</sup> for  $O_2$ . For completeness we also show the MO-ADK results. All the results are normalized at their peak values. In all the cases the effect of core polarization was found to be quite insignificant. In particular, at the peak ionization, the account for the dynamic core polarization leads to an reduction of ionization rates by about 13% for  $N_2$ , 20% for  $CO_2$ , and 1% for  $O_2$ . The position of

the peak remains unchanged for  $N_2$  and  $O_2$ , and slightly changes for  $CO_2$ . The MO-ADK results are also in good agreements with the TDSE results for  $N_2$  and  $O_2$  and experiments [18, 19]. For  $CO_2$ , the peak ionization from the TDSE occurs near  $\beta = 40^\circ$ , in a better agreement with Pavicic *et al* [19], than the MO-ADK result. Recall that Pavicic *et al* [19] found a very narrow peak near  $\beta = 45^\circ$  that was not reproduced by any theoretical calculations so far [21, 44, 46, 47]. We further remark that Majety and Scrinzi recently attributed the shift in the peak position to near  $45^\circ$  for tunneling ionization from  $CO_2$  as due to dynamic exchange effect, at least for the static field limit [48].

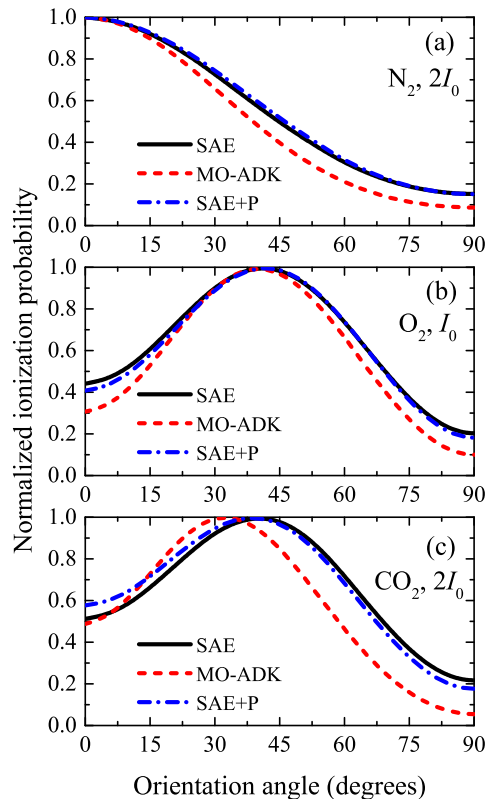


FIG. 6. (Color online) (a): The normalized ionization probability from the TDSE with and without the dynamic core polarization for  $N_2$ , labeled as SAE and SAE+P, respectively. The MO-ADK result is also shown. (b) and (c): same as (a), but for  $O_2$ , and  $CO_2$ , respectively. The calculations were done with 800 nm laser with an intensity of  $2 \times 10^{14}$  W/cm<sup>2</sup> for  $N_2$  and  $CO_2$ , and  $10^{14}$  W/cm<sup>2</sup> for  $O_2$ .

## IV. CONCLUSIONS

We have studied the effect of permanent dipole on the tunneling ionization for polar molecules in intense laser fields on a  $Z_1Z_2$  model as well as CO and NO. We found that account for the Stark effect in the MO-ADK theory leads to an improved agreement with the numerical solution of the TDSE at the level of a single-active electron approximation, although the Stark-corrected theories in general tend to overestimate the effect of the permanent dipole. For the tunneling regime, a possible improvement might come from an approach proposed by Tolstikhin and collaborators, by including the first order correction to the WFAT [49]. Extension to the multiphoton regime is needed for more quantitative treatment of polar molecules. Clearly, high quality results for angle-dependent ionization would be essential for correct retrieval in dynamic imaging techniques such as the LIED and HHS, which are based on the rescattering physics.

We further showed that account for the dynamic polarization of core electrons induced by the laser field is critical for CO molecule, but insignificant for NO,  $N_2$ ,  $O_2$ , and  $CO_2$ . Clearly, further theoretical and experimental investigations are needed to shed light into this critically important problem.

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