

## Analysis of angular dependence of strong-field tunneling ionization for CO<sub>2</sub>

Song-Feng Zhao,<sup>1,2</sup> Cheng Jin,<sup>1,2</sup> Anh-Thu Le,<sup>1</sup> T. F. Jiang,<sup>1,3</sup> and C. D. Lin<sup>1</sup>

<sup>1</sup>*J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506-2604, USA*

<sup>2</sup>*College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou, Gansu 730070, People's Republic of China*

<sup>3</sup>*Institute of Physics, National Chiao-Tung University, Hsinchu 30010, Taiwan*

(Received 9 September 2009; published 17 November 2009)

We analyzed the discrepancy of the angular dependence of strong-field ionization for CO<sub>2</sub> among the different theoretical calculations and experiments. Using a more accurate ground-state wave function of CO<sub>2</sub> in the asymptotic region, we showed that the accuracy in the earlier tunneling ionization theory of Tong *et al.* [Phys. Rev. A **66**, 033402 (2002)] is much improved. We also concluded that the angular dependence deduced from the experiment of Pavičić *et al.* [Phys. Rev. Lett. **98**, 243001 (2007)] appears to be too narrowly distributed.

DOI: 10.1103/PhysRevA.80.051402

PACS number(s): 33.80.Rv, 42.50.Hz

Ionization of molecules in strong field is the first step to interesting strong-field phenomena such as high-order harmonic generation, high-energy above-threshold ionization, and dynamic imaging of molecules by the rescattering electrons. Fundamental knowledge to these processes is the angular dependence of ionization probability  $P(\theta)$  for a molecule fixed in space, where  $\theta$  is the angle between the molecular axis and the direction of laser's electric field. Since molecules are generally not aligned nor oriented in the gas phase, such measurements are not direct. In recent years, the angular dependence  $P(\theta)$  for some simple molecules like H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CS<sub>2</sub>, and CO have been reported [1–7]. In these measurements,  $P(\theta)$  has to be retrieved from the experimental data under some assumptions. Theoretically,  $P(\theta)$  can in principle be calculated directly from solving the time-dependent Schrödinger equation (TDSE). However, it is rather difficult to achieve accurate numerical results for such complex systems and the accuracy of the calculation cannot be easily assessed.

Despite these limitations, molecular tunneling ionization theory [8] based on the model of Ammosov, Delone, and Krainov (ADK) [9], i.e., the MO-ADK theory, or the strong-field approximation (SFA) [10,11] appear to agree well with each other and with experimental data for most molecules that have been studied. However, there is one important exception—the CO<sub>2</sub> molecule. Such discrepancy was brought out in the experiment of Pavičić *et al.* [5] where the peak of  $P(\theta)$  was found to be at about 46°, while based on the original MO-ADK theory, the peak was predicted at 25°. More importantly, experimental data indicate that the ionization probability is distributed over a much narrower angular range than the MO-ADK theory predicted. The possible problem of MO-ADK theory for CO<sub>2</sub> has been noted already earlier [12]. While the normalized  $P(\theta)$  obtained from MO-ADK agrees with that from SFA (if the probabilities are renormalized) for most molecules, this is not the case for CO<sub>2</sub>.

The discrepancy found in Pavičić *et al.* [5] has generated a flurry of new theoretical calculations. These more elaborate calculations obtained ionization probability by solving the TDSE for each alignment angle, within the single active electron model [13] or including the many-electron effect [14]. These calculations were able to obtain the peak position

of  $P(\theta)$  quite close to the experimental observation but not the narrowness in its angular width. These calculations also do not offer any hint why the MO-ADK theory fails for CO<sub>2</sub> but not for most of other systems. Based on these newer calculations, does it imply that similar complicated calculations should be carried out for all molecules? Here we offer a different interpretation. We identified the main reason for the failure of the earlier MO-ADK theory to the inaccurate molecular wave function used for CO<sub>2</sub>, while the cause for the failure of the theory to reproduce experimental narrow angular distribution of Pavičić *et al.* [5] may lie in the experiment.

First we explain what was the problem with the earlier version of MO-ADK theory for CO<sub>2</sub>. Recall MO-ADK is a generalization of the tunneling ionization theory of ADK [9] which was initially used to describe tunneling ionization of atoms. In this theory, static tunneling ionization rate is given analytically, and the rate depends only on the binding energy of the electron and the ground-state wave function in the asymptotic region. For atomic targets, the asymptotic wave function (at large  $r$ ) can be expressed as

$$\Psi^m(\vec{r}) \simeq C_l Y_{lm}(\hat{r}) r^{Z_c/\kappa-1} e^{-\kappa r}. \quad (1)$$

If the quantization axis is chosen to be along the direction of laser's polarization, then  $m=0$  is dominant since it gives a much larger electron density along the direction of the laser's electric field. In this equation,  $Z_c$  is the asymptotic charge,  $Y_{lm}$  is the spherical harmonics, and  $\kappa = \sqrt{2I_p}$ , where  $I_p$  is the ionization energy. To generalize ADK theory to molecules where the molecular axis is parallel to the polarization axis, one can expand the molecular wave function at large  $r$  similar to Eq. (1),

$$\Psi^m(\vec{r}) \simeq \sum_l C_l Y_{lm}(\hat{r}) r^{Z_c/\kappa-1} e^{-\kappa r}. \quad (2)$$

Here the asymptotic wave function is written in a single-center expansion form. Using this expansion, the analytical ADK rate can be generalized to molecular targets directly. For molecules that are not aligned along the laser polarization direction, the coefficient in the ADK theory is obtained

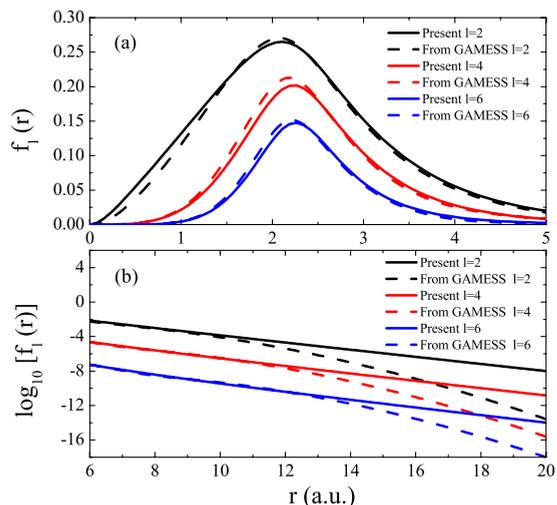


FIG. 1. (Color online) Partial wave radial function of  $\text{CO}_2$ : (a) small- $r$  region; (b) large- $r$  region. The solid lines are from the present results, and dashed lines are calculated with GAMESS code. For clarity, in (b), the radial function for  $l=4$  ( $l=6$ ) is divided by  $10^2$  ( $10^4$ ).

by a simple rotation. More about the MO-ADK theory is given in Tong *et al.* [8].

The MO-ADK theory has many attractive features. It is simple. Once the coefficients  $C_l$  are obtained, the angular dependence can be calculated for any laser intensity and any alignment angle. Since it is an expression for the static rate, it does not depend on laser's wavelength nor on pulse duration. The MO-ADK theory has been shown to be quite accurate in the tunneling regime for many molecules. Corrections to ADK near the over-the-barrier region [15] and for large polarizable targets [16] have also been reported.

In view of the general success of the MO-ADK theory, we now return to the question why it fails so “miserably” for  $\text{CO}_2$ ? Since the distance between the two oxygen atoms in  $\text{CO}_2$  is about twice that in  $\text{O}_2$ , could the simple MO-ADK tunneling model no longer hold? Before drawing such a conclusion, however, it is prudent to check whether the parameters  $C_l$  in Eq. (2) have been obtained accurately.

Originally in Tong *et al.* [8], the parameters  $C_l$  are obtained from multiple scattering theory [17]. However, molecular wave functions are more accessible using packages such as GAMESS or GAUSSIAN. The ground-state wave function of the highest occupied molecular orbital can be easily calculated from such packages and fit to the form of Eq. (2)

in the asymptotic region to find the coefficients  $C_l$ . This procedure was used by Le *et al.* for  $\text{CO}_2$  [18] and by Kjeldsen and Madsen [19] for other molecules. The MO-ADK theory requires that the wave function be accurate in the asymptotic region. In GAMESS and GAUSSIAN, molecular orbitals are expanded in terms of Gaussian basis functions. These basis functions do not have the correct form of Eq. (2) in the large- $r$  region. Thus the  $C_l$  coefficients depend sensitively on the region of  $r$  where the parameters are extracted, as well as on the basis set used in the calculation. Note that this limitation is not easily overcome by increasing the number of Gaussian basis functions included.

To obtain accurate orbital wave function in the asymptotic region, we “resolve” the wave function for each orbital in the single active electron approximation following the general description of the density-functional theory (DFT), including exchange interaction and correlation effect [20,21]. This is also the procedure used recently by Abu-samha and Madsen [12]. In fact, we used the  $\text{CO}_2$  potential kindly provided by them. With such a two-center potential, we resolve the eigenvalue and eigenfunction for the ground  $\pi_g$  orbital using basis functions consisting of  $B$ -spline functions. Since it is a single electron calculation, the number of basis functions can be much enlarged. In Fig. 1(a), we show the radial wave functions in the inner region for the first three partial waves and compared to the ones from GAMESS directly. They agree quite well. In Fig. 1(b), the same functions in the large- $r$  region are shown. For each component, the wave function clearly displays the exponential decay form of Eq. (2). Those obtained from GAMESS, however, exhibit oscillations and drop much faster like a Gaussian function, reflecting the nature of the Gaussian basis functions used in the GAMESS package. Thus parameters  $C_l$  cannot be accurately obtained from wave functions calculated from GAMESS or from GAUSSIAN codes directly.

In Table I, we compare the coefficients,  $C_{21}$ ,  $C_{41}$ , and  $C_{61}$ —the first three coefficients for the  $\pi_g$  orbital of  $\text{CO}_2$  obtained directly from the GAMESS wave function and from the newly calculated one. Note that the ratio of the first two coefficients for the new wave function is 6.8, while from GAMESS, the ratio is only 1.7. Using these coefficients, in Fig. 2, we show the normalized alignment dependence of the ionization rate,  $P(\theta)$ . The peak of  $P(\theta)$  from the calculation is now at about  $34^\circ$  instead of  $25^\circ$  from the original MO-ADK. The new one is much closer to the peak at  $38^\circ$  predicted by SFA [12].

How are the new MO-ADK result compares to other recent calculations and experiment? In Fig. 3(a), we show the

TABLE I. The newly fitted  $C_l$  coefficients vs the old ones, for  $\text{CO}_2$  ( $m=1$ ) and  $\text{H}^+_2$  ( $m=0$ ). Old data are from Refs. [8,18].

Molecule	$I_p$ (eV)	$R$ (Å)	$C_{0m}$	$C_{2m}$	$C_{4m}$	$C_{6m}$
$\text{CO}_2(\pi_g)$	13.769	1.163	1.27	0.188	0.014	
				2.88	1.71	0.427
$\text{H}^+_2(\sigma_g)$	29.99	1.058	4.52	0.62	0.03	
			4.37	0.05	0.0	[8]

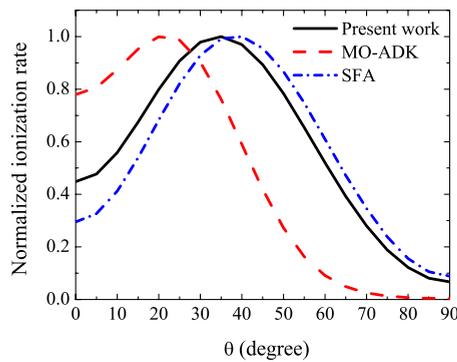


FIG. 2. (Color online) The normalized alignment dependence of ionization rate of  $\text{CO}_2$ . The laser intensity is  $2 \times 10^{14}$  W/cm $^2$ . MO-ADK and SFA from [12].

normalized  $P(\theta)$  from the present MO-ADK theory, from the TDSE calculation of Abu-samha and Madsen [13], and from Son and Chu [14] using multielectron time-dependent DFT theory, with the experimental data of Pavičić *et al.* [5], for peak laser intensity of  $1.1 \times 10^{14}$  W/cm $^2$ . The angle where  $P(\theta)$  peaks from the experiment is about  $45^\circ$ , the present MO-ADK predicts the peak at  $34^\circ$ , while the other two calculations are at  $42^\circ$  and  $40^\circ$ , respectively. Compared to the experiment, the present MO-ADK prediction is still inferior. In view of the simplicity of the MO-ADK theory and its approximate nature, we consider such discrepancy acceptable. In other words, the alignment dependence of ionization rates for  $\text{CO}_2$  predicted using the MO-ADK tunneling theory is still correct, at least semiquantitatively. In Fig. 3(a), however, we note that the angular widths  $P(\theta)$  predicted from all the theories are all much broader than the experimental one. We consider such difference too large and not acceptable.

In the experiment of Pavičić *et al.* [5], a pump beam was

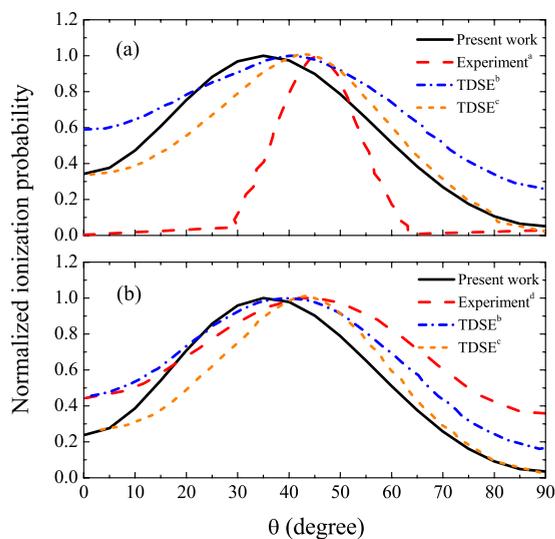


FIG. 3. (Color online) The normalized alignment dependence of ionization probability of  $\text{CO}_2$ . (a) Laser intensity is  $1.1 \times 10^{14}$  W/cm $^2$ ; (b) laser intensity is  $0.5 \times 10^{14}$  W/cm $^2$ . Note that  $0.56 \times 10^{14}$  and  $0.3 \times 10^{14}$  W/cm $^2$  were used in [13,6], respectively. Experiment $^a$  from [5], TDSE $^b$  from [14], TDSE $^c$  from [13], and Experiment $^d$  from [6].

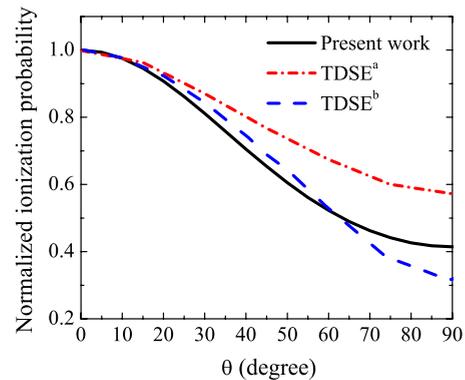


FIG. 4. (Color online) Normalized alignment dependence of ionization probability of  $\text{H}_2^+$  at laser intensity of  $5 \times 10^{14}$  W/cm $^2$ . TDSE $^a$  from [22] and TDSE $^b$  from [23].

first used to partially align molecules. The angular (or alignment) distributions of the molecules were first determined by ionizing molecules with an intense circularly polarized laser pulse. A linearly polarized light is then used to measure the alignment dependence of the ionization rate where the polarization axis of the laser with respect to the molecular axis is varied. To extract the fixed-in-space ionization probability,  $P(\theta)$ , experimental data have to be deconvoluted. Similar alignment dependence  $P(\theta)$  for  $\text{CO}_2$  has also been reported by Thomann *et al.* [6] recently at a peak intensity of  $0.3 \times 10^{14}$  W/cm $^2$ , i.e., at about quarter the peak intensity of Pavičić *et al.* [5]. Their results, together with theoretical calculations, are shown in Fig. 3(b). In this case, the experimental data has a very broad angular distribution, consistent with all the theoretical calculations. The peak angle from the experiment is at about  $43^\circ$ . The two TDSE calculations and the new MO-ADK result are all close to this value. Note that the narrow angular width in Pavičić *et al.* [5] is inconsistent with the broad one reported in Thomann *et al.* [6]. In particular, one expects angular width to become slightly broader at higher laser intensities. Based on these comparisons, we suggest that it is appropriate to re-examine the experiment at the higher intensity used in Pavičić *et al.* [5].

Finally, can one draw some general conclusions on the differences among the three theoretical calculations? If all the calculations are done “exactly” within the approximation made in the model, then one may interpret the difference of MO-ADK from Abu-samha and Madsen [13] as the limitation of the tunneling model since both theories start with the same one-electron Hamiltonian. In Abu-samha and Madsen [13], the big difference between the “old” MO-ADK result and their calculation was attributed to the importance of intermediate resonance states included in the TDSE calculation. However, comparing their results with the “new” MO-ADK results, as shown in Fig. 3, the discrepancy is not that large except that the MO-ADK theory tends to distribute its  $P(\theta)$  at smaller angles. Similarly, the difference between the results of Son and Chu and of Abu-samha and Madsen may be attributed to many-electron effect. However, all of these conclusions should be taken with caution. If TDSE can be solved “exactly” within the one-electron model or the many-electron model (within the multielectron DFT), then such a

conclusion is valid. However, direct numerical solution of TDSE for aligned molecules is still very difficult, even for the simplest one-electron  $\text{H}_2^+$ . In Fig. 4, we compare the normalized ionization probability of  $\text{H}_2^+$  from solving the TDSE at the intensity of  $5 \times 10^{14}$  W/cm<sup>2</sup> by Kjeldsen *et al.* [22] and by Kamta *et al.* [23]. The two TDSE calculations reveal significant discrepancy at large angles. Their difference is about the same as the difference between the TDSE and the MO-ADK. We comment that the MO-ADK results presented in Fig. 4 are obtained using the newly fitted coefficients (see Table I). As experimental data and elaborate calculations for  $P(\theta)$  become increasingly available, all the coefficients in the MO-ADK theory of Tong *et al.* [8] will have to be re-evaluated again using the present method.

In summary, in an effort to resolve the prevailing discrepancy in the alignment dependence of strong-field ionization rates in  $\text{CO}_2$  between MO-ADK theory and the experimental

data of Pavičić *et al.* [5], we returned to revisit the MO-ADK theory. We found that the major discrepancy can be removed if the parameters in the MO-ADK theory are calculated from wave functions which have the correct asymptotic behavior. The latter is not possible if one uses wave functions directly generated from GAMESS or GAUSSIAN codes. We also concluded that the angular width reported in the measurement of Pavičić *et al.* [5] appears to be too narrow. Their result is also in disagreement with the recent data of Thomann *et al.* [6].

We thank Lars Madsen and Mahmoud Abu-samha for providing the model potential used in this work. This work was supported in part by Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, (U.S.) Department of Energy. S.-F.Z. was also supported by the National Natural Science Foundation of China under Grant No. 10674112.

- 
- [1] I. V. Litvinyuk *et al.*, Phys. Rev. Lett. **90**, 233003 (2003).
  - [2] A. S. Alnaser *et al.*, Phys. Rev. Lett. **93**, 113003 (2004).
  - [3] A. S. Alnaser *et al.*, Phys. Rev. A **71**, 031403(R) (2005).
  - [4] A. Staudte *et al.*, Phys. Rev. Lett. **102**, 033004 (2009).
  - [5] D. Pavičić, K. F. Lee, D. M. Rayner, P. B. Corkum, and D. M. Villeneuve, Phys. Rev. Lett. **98**, 243001 (2007).
  - [6] I. Thomann, R. Lock, V. Sharma, E. Gagnon, S. T. Pratt, H. C. Kapteyn, M. M. Murnane, and W. Li, J. Phys. Chem. A **112**, 9382 (2008).
  - [7] V. Kumarappan *et al.*, Phys. Rev. Lett. **100**, 093006 (2008).
  - [8] X. M. Tong, Z. X. Zhao, and C. D. Lin, Phys. Rev. A **66**, 033402 (2002).
  - [9] M. V. Ammosov, N. B. Delone, and V. P. Krainov, Zh. Eksp. Teor. Fiz. **91**, 2008 (1986) [Sov. Phys. JETP **64**, 1191 (1986)].
  - [10] J. Muth-Böhm, A. Becker, and F. H. M. Faisal, Phys. Rev. Lett. **85**, 2280 (2000).
  - [11] T. K. Kjeldsen and L. B. Madsen, J. Phys. B **37**, 2033 (2004).
  - [12] V. H. Le, N. T. Nguyen, C. Jin, A. T. Le, and C. D. Lin, J. Phys. B **41**, 085603 (2008).
  - [13] M. Abu-samha and L. B. Madsen, Phys. Rev. A **80**, 023401 (2009).
  - [14] S. K. Son and Shih-I. Chu, Phys. Rev. A **80**, 011403(R) (2009).
  - [15] X. M. Tong and C. D. Lin, J. Phys. B **38**, 2593 (2005).
  - [16] T. Brabec, M. Côté, P. Boulanger, and L. Ramunno, Phys. Rev. Lett. **95**, 073001 (2005).
  - [17] D. Dill and J. L. Dehmer, J. Chem. Phys. **61**, 692 (1974).
  - [18] A.-T. Le, X. M. Tong, and C. D. Lin, J. Mod. Opt. **54**, 967 (2007).
  - [19] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A **71**, 023411 (2005).
  - [20] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).
  - [21] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
  - [22] T. K. Kjeldsen, L. A. A. Nikolopoulos, and L. B. Madsen, Phys. Rev. A **75**, 063427 (2007).
  - [23] G. L. Kamta and A. D. Bandrauk, Phys. Rev. A **71**, 053407 (2005).