Vol 10 No 9, September 2001
1009-1963/2001/10(09)/0814-07

Chinese Physics

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FIELD IONIZATION OF MOLECULES IN AN INTENSE LASER FIELD*

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(Received 9 April 2001; revised manuscript received 24 April 2001)

In order to predict the field ionization probabilities, the accurate *ab initio* electrostatic potential of molecules has to be calculated. However, the calculation of the full *ab initio* electrostatic potential of molecules is complicated, even impossible for some larger molecules with low symmetry. Here, we present a semi-empirical model to treat the field ionization of molecules in an intense laser field. In this model, a modified Coulomb potential is used to take the place of the complicated *ab initio* electrostatic potential of molecules. The analytic equations of the Keldysh adiabatic parameter using the Coulomb potential and the modified Coulomb potential have first been given. Using our semi-empirical model, we have calculated the field ionization probabilities and the Keldysh adiabatic parameters of O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6 in an intense laser field. The results agree excellently with the calculations using the *ab initio* electrostatic potential of molecules. As the modified parameter for the Coulomb potential can be found from experimental measurements, the field ionization mechanism of molecules can be immediately predicted with our semi-empirical model.

Keywords: field ionization, Keldysh adiabatic parameter, *ab initio* calculation
PACC: 3280F, 3120A, 0365

With the development of chirped pulse amplification technology, the electric field of a focused ultrashort laser beam can match the molecular Coulomb field felt by valence electrons. The study of photoionization of molecules induced by such intense laser fields has become of considerable interest in recent years.[1−23] The ionizationc mechanisms have been divided into two regimes: multiphoton ionization (MPI) and field ionization (FI). FI includes tunnelling ionization (TI) and barrier suppression ionization (BSI).

A theory on the ionization mechanism of atoms in an intense external electronic field was first proposed by Keldysh in 1964.[24] In the theory, the Keldysh adiabatic parameter γ is defined as the ratio of the laser frequency to the tunnelling frequency. If γ is much larger than unity, MPI dominates. Otherwise, TI plays the main role.

To the field ionization of atoms and a few diatomic molecules, various theories have been applied.[24−30] While for the molecules, which have a variety of structures and orbits, the existing theories developed for atoms cannot predict their ionization mechanism in an intense laser field.

Recently, molecular-structure-based model[19,20] and molecular-orbit-based model[31] have been proposed to treat the field ionization of polyatomic molecules. However, the calculation of the accurate *ab initio* electrostatic potential of molecules is complicated, even impossible for some large molecules with low symmetry. The complexity hinders the utilization of these models. Up to now, the study of ionization of polyatomic molecules has still concentrated on experimental explorations. Due to the limited quantificational theoretical calculation, the ionization mechanism is still controversial, especially when the γ value is near unity. For example, the ionization of NO_2 under the laser intensity of a few 10^{13}W/cm^2 was described with multiphoton processes by the Glasgow group.[32] While Mathur *et al.*[33] insist that the large NO_2^+ parent ions should be produced via field ionization. In this paper, we present a semi-empirical model to treat the field ionization of molecules. In the model, a modified Coulomb potential is used to describe the electrostatic potential of the valence electron in the highest occupied molecular orbit (HOMO). The field ionization probability and the Keldysh adiabatic parameter γ of molecules can be easily calculated and the field ionization mechanism can be easily predicted using our new model.

The suggestion that a modified Coulomb poten-

*Project supported by the Special Foundation for State Major Basic Research Program of China (Grant No. G1999075207), the National Natural Science Foundation of China (Grant Nos. 19884001 and 19525412), and the China Postdoctoral Science Foundation.

tial is used to replace the *ab initio* electrostatic potential of molecules is based on the following two reasons. One reason is that the electrons in HOMO can move freely within the inner classical turning points of the *ab initio* electrostatic potential. It is therefore unnecessary to know the detailed shape within the inner classical turning points of the *ab initio* electrostatic potential when the field ionization probability and the Keldysh adiabatic parameter γ are calculated. The other reason is that the electrostatic potential of the valence electron approaches a pure Coulomb potential $-1/r$ at a relatively larger distance r due to the shielding of the inner-shell electrons. Hence, a modified Coulomb potential is used to take the place of the *ab initio* electrostatic potential of molecules in our model. The validity of our model has been tested by comparing the field ionization probability and the Keldysh adiabatic parameter γ of O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6 calculated using the molecular-orbit-based model[31] and our new model. The choice of these six molecules is due to their different orbit structures.

In the molecular-orbit-based model,[31] only the electron in HOMO is assumed to be pulled out from the molecule along a vector of the densest distribution of the electron charge. According to the photoelectron spectroscopic data, the HOMOs are the antibonding π_g orbit for O_2,[34] the bonding σ_g orbit for N_2,[34] the non-bonding orbit of the sulphur atom n_s for SO_2,[35] the C—C π orbit for C_2H_4,[36] the C—N π orbit for CH_3CN[37] and the conjugated π orbit for C_6H_6.[36] The electrostatic potential of the above molecules can be calculated by the *ab initio* method according to the molecular-orbit-based model. Figure 1(a) shows the *ab initio* electrostatic potential of C_6H_6. The arrow denotes the vector along which the valence electron is pulled out. When the laser field is applied on the molecule, the electrostatic potential will be distorted and a barrier will be formed on the one side of the potential (see Fig.1(b)). The laser intensity (I) dependence of the electric field ε is given by $\varepsilon = \sqrt{I}$. Atomic units are used throughout this paper unless otherwise stated.[38] If the laser field surpasses a critical value ε_{th}, the energy of the valence electron is higher than the height of the potential barrier (see Fig.1(c)). The critical value ε_{th} is called the threshold intensity. BSI occurs when the laser field is larger than the threshold intensity. The field ionization probability is assumed to be unity when ionization enters the BSI regime. The calculated ε_{th} values using the molecular-orbit-based model are 0.049, 0.074, 0.051, 0.037, 0.042 and 0.025 for O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6, respectively.

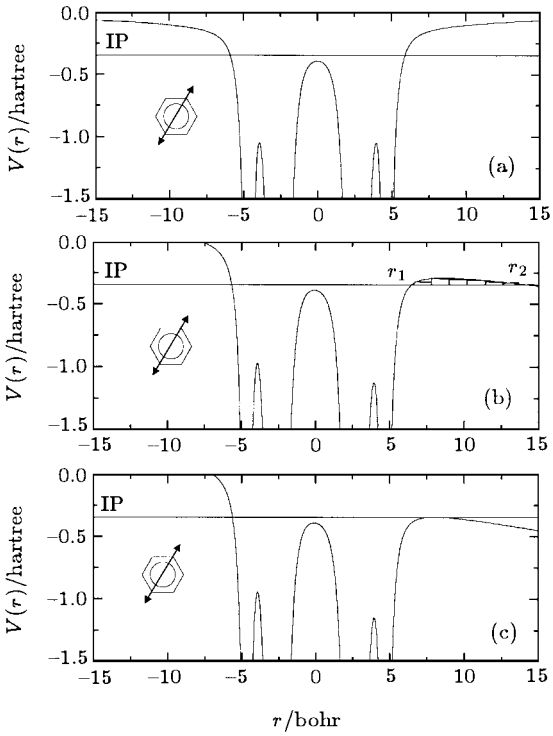


Fig.1. The *ab initio* electrostatic potential for C_6H_6 at a laser intensity of (a) 0, (b) 1.3×10^{13}W/cm^2, and (c) 2.3×10^{13}W/cm^2. The ionization in the cases of (b) and (c) corresponds to tunnelling ionization and barrier suppression ionization.

When the laser field is lower than the threshold intensity, the field ionization probability is the tunnelling efficiency of the electron through the barrier, which can be calculated by the Wentzel–Kramers–Brillouin (WKB) theory[39] and quantum mechanics (QM) theory[40] individually. The WKB tunnelling probability is:

$$w = \exp\left[-2\int_{r_1}^{r_2}[2(E-V(r))]^{1/2}\mathrm{d}r\right], \qquad (1)$$

where $V(r)$ is the perturbed electrostatic potential, E is the ionization potential of the molecule, and r_1 and r_2 are the classical turning points (see Fig.1(b)) determined by the ionization potential and the field-perturbed electrostatic potential. But the requirement of the WKB approximation can be met only when the ionization probability is less than $1/e$.[39]

The QM theory[40] overcomes the limitation of the WKB theory. In this theory, the potential barrier is approximated by a series of rectangular potential barriers (see Fig.1(b)). The tunnelling probability of electrons through a rectangular potential barrier can be

accurately obtained by solving the Schrödinger equation. Due to the continuity of the wave function and its first-order derivative at the boundary, the field ionization probability can be numerically calculated in the whole field ionization range. Kong *et al.*[31] calculated the field ionization probability of three aliphatic ketones by using this theory.

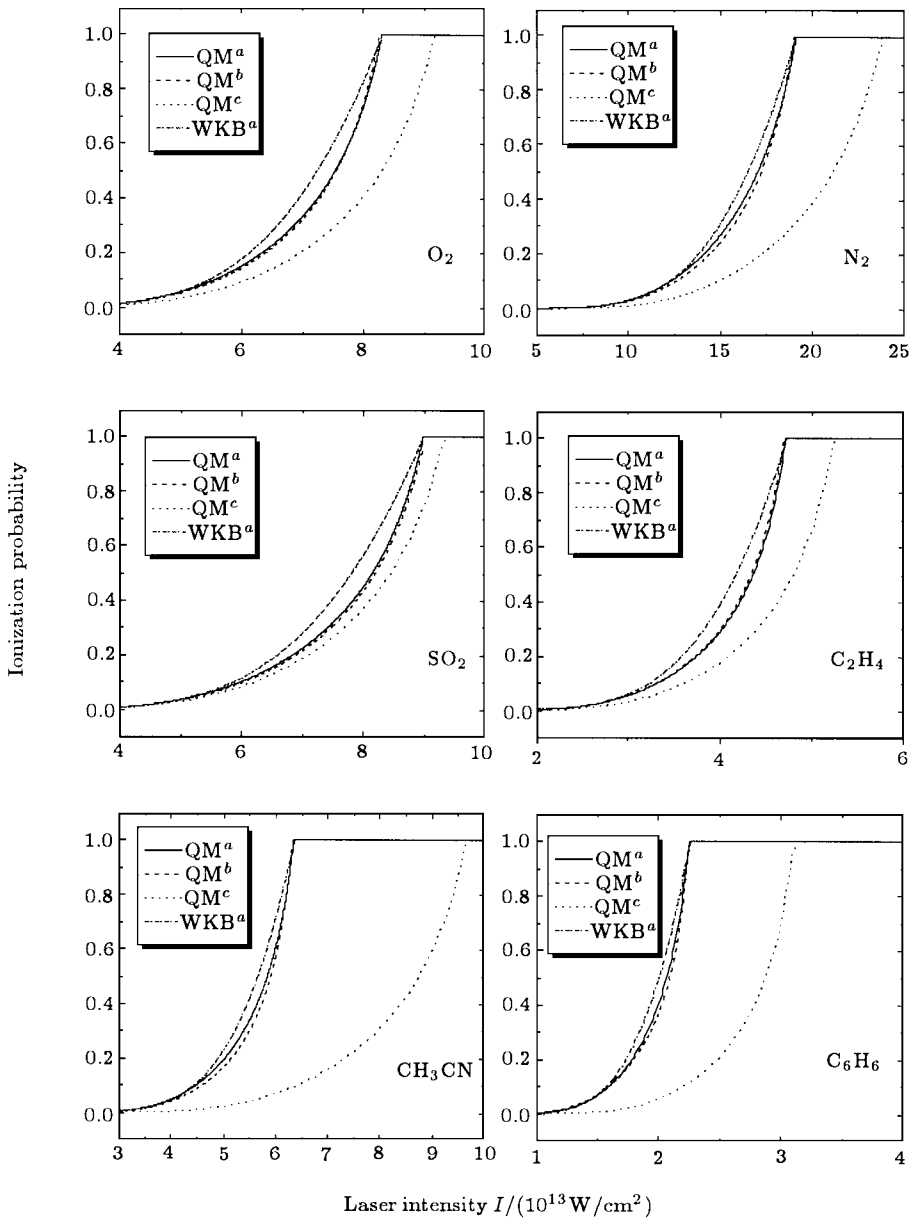


Fig.2. Laser intensity dependence of the field ionization probability. QM denotes the quantum mechanics theory and WKB denotes the Wentzel–Kramers–Brillouin theory. *a*, *b* and *c* represent the *ab initio* electrostatic potential, the modified Coulomb potential and the Coulomb potential, respectively.

The ionization probabilities calculated by the QM and WKB theories using the *ab initio* electrostatic potentials are shown by the solid and the dot-dashed lines in Fig.2, respectively. It can be seen that the value calculated by using the WKB theory agrees well with that calculated by the QM theory when the field ionization probability is low.

In our model, a modified Coulomb potential is used to replace the *ab initio* electrostatic potential of molecules. Thus, for the molecules in an intense laser field, the real potential felt by the valence electron is the superposition of the modified Coulomb potential and the laser field. This can be written as:

$$V(r) = -\frac{P}{|r|} - \varepsilon \cdot r, \tag{2}$$

where P is the modified parameter, which can be obtained by the assumption that the threshold intensities derived from the modified Coulomb potential equal that derived from the *ab initio* electrostatic potential. The P values should therefore be determined by the following equation:

$$P = \frac{E^2}{4\varepsilon_{\rm th}}, \tag{3}$$

where $\varepsilon_{\rm th}$ is the threshold intensity calculated using the *ab initio* electrostatic potential. The modified parameters for O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6 are tabulated in Table 1.

Table 1. Properties and values measured for O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6.

Molecules	Threshold intensity $\varepsilon_{\rm th}$ for BSI			
	Ionization potential	Coulomb potential	*ab initio* electrostatic potential	Modified parameter P
O_2	0.452	0.051	0.049	1.04
N_2	0.574	0.082	0.074	1.11
SO_2	0.454	0.052	0.051	1.01
C_2H_4	0.393	0.039	0.037	1.04
CH_3CN	0.458	0.053	0.042	1.25
C_6H_6	0.345	0.030	0.025	1.19

Once the modified Coulomb potential is established, the field ionization probability can be calculated by using the QM theory. The results are shown by the dashed lines in Fig.2. It is clear that the ionization probability calculated using the modified Coulomb potential agrees very well with that calculated by using the *ab initio* electrostatic potential. In order to determine whether the modified Coulomb potential is necessary, we calculate the ionization probabilities in terms of the QM theory using the Coulomb potential. The results are also shown in Fig.2 by the dotted lines. This clearly indicates that an obvious discrepancy exists between the ionization probabilities calculated by using the Coulomb potential and the *ab initio* electrostatic potential. Therefore, the modification of the Coulomb potential is necessary to predict the accurate field ionization probability of molecules in an intense laser field.

Certainly, the modified parameter P can also be determined from the experimental results. Given different values of P, we can calculate a set of laser intensity dependence of field ionization probabilities. The ions produced in the intense laser field are directly proportional to the integration of the ionization probability $P(I)$ over the time and space of the laser pulse. The total ion yield in a laser pulse is

$$S = \alpha c \int_{\rm time} \int_{\rm space} P(I) {\rm d}v {\rm d}t, \tag{4}$$

where α is the instrument sensitivity, c is the concentration of samples, ${\rm d}v$ is the volume between the iso-intensity shells of the intensity I and $I + {\rm d}I$. Thus we can obtain the curves of the ion yield versus laser intensity for different modified parameter PS. Comparing the experimentally measured ion yield versus laser intensity with the theoretical curves, the optimal modified parameter P is obtained and the field ionization probability is therefore accurately determined.

The Keldysh adiabatic parameter γ is an important criterion to determine the ionization mechanism of atoms and molecules in an intense laser field.[24] For simplicity, Keldysh assumed that the potential felt by valence electrons is the zero-range potential. When a laser field is applied to the atom, a potential barrier is created. The length of the barrier l can be expressed as:

$$l = \frac{E}{e\varepsilon}, \tag{5}$$

where e is the electron charge. Substituting Eq.(5) into the definition of the Keldysh adiabatic parameter γ, we obtain:

$$\gamma = \frac{\omega\sqrt{2m_{\rm e}E}}{e\varepsilon}, \tag{6}$$

where ω is the angular frequency of the laser field, and $m_{\rm e}$ is the mass of the electron. If γ is much larger than unity, then multiphoton ionization dominates. Otherwise, the field ionization dominates.

Even if the zero-range potential and the original formula for the Keldysh adiabatic parameter are

widely used, the zero-range potential is too simple, even for simple diatomic molecules.[41] Here, we calculate the Keldysh adiabatic parameter γ using the zero-range potential, the Coulomb potential and the modified Coulomb potential. The results are compared with the calculations using the *ab initio* electrostatic potential. The equations for calculating the length of the barrier l and the Keldysh adiabatic parameter γ are tabulated in Table 2. Among these, the analytic equations using the Coulomb potential and the modified Coulomb potential are given for the first time to the best of our knowledge.

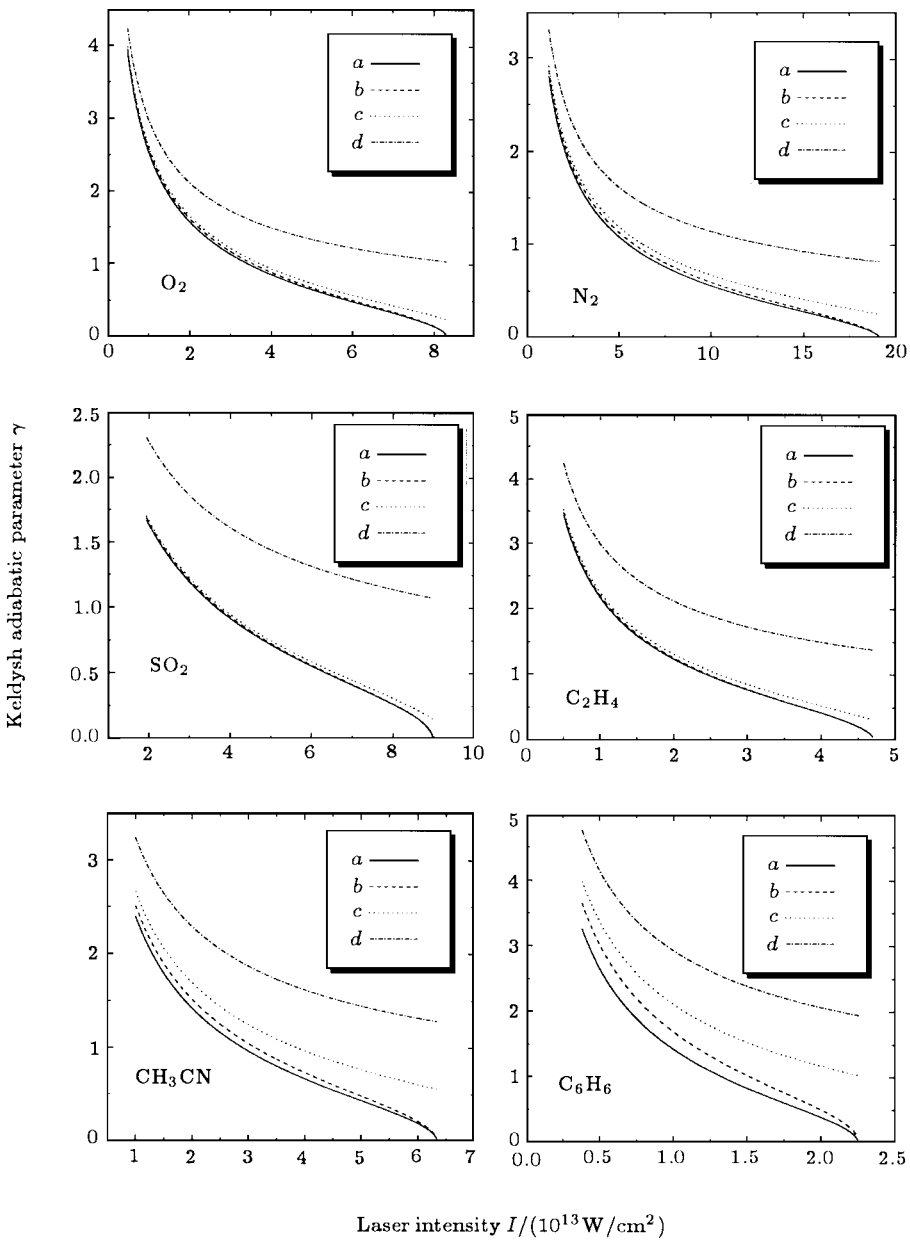


Fig.3. Laser intensity dependence of the Keldysh adiabatic parameter γ for four different potentials. Curves *a*, *b*, *c* and *d* represent the results obtained using the *ab initio* electrostatic potential, the modified Coulomb potential, the Coulomb potential and the zero-range potential, respectively.

Figure 3 shows the laser intensity dependence of the Keldysh adiabatic parameter γ for O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6 in an intense laser field using four different potentials. The angular frequency ω of the laser field is taken to be 0.057 atomic unit and the laser wavelength is 800nm. It is clear that the γ value calculated using the zero-range potential is much higher than that calculated with the *ab initio* electrostatic potential for all six molecules. The γ value derived from the Coulomb potential approaches

Table 2. Equations for calculating l and γ using four different potentials.

Potential	Length of potential barrier l	Keldysh adiabatic parameter γ
Zero-range potential	$\frac{E}{e\varepsilon}$	$W_{\text{laser}}\frac{(2m_eE)^{1/2}}{e\varepsilon}$
Coulomb potential	$\frac{(E^2-4e\varepsilon)^{1/2}}{e\varepsilon}$	$W_{\text{laser}}\left[\frac{2m_e(E^2-4e\varepsilon)}{E}\right]^{1/2}\frac{1}{e\varepsilon}$
Modified Coulomb potential	$\frac{(E^2-4Pe\varepsilon)^{1/2}}{e\varepsilon}$	$W_{\text{laser}}\left[\frac{2m_e(E^2-4Pe\varepsilon)}{E}\right]^{1/2}\frac{1}{e\varepsilon}$
ab initio electrostatic potential	determined by $V_{\text{field-free}}-e\varepsilon r=-E$	substitute l into $\gamma=2W_{\text{laser}}l\frac{1}{(2E/m_e)^{1/2}}$

that derived from the *ab initio* electrostatic potential for O_2, N_2, SO_2 and C_2H_4, and exhibits a deviation for CH_3CN and C_6H_6. Therefore, the Coulomb potential based adiabatic parameter roughly describes the ionization mechanism. While the γ value derived from the modified Coulomb potential accords with that derived from the *ab initio* electrostatic potential for all the six molecules. The results further support the suggestion in our model that a modified Coulomb potential is enough to predict the ionization mechanism for molecules in an intense laser field.

In conclusion, we have presented a semi-empirical model to treat the field ionization of molecules in an intense laser field. In the model, a modified Coulomb potential is used to take the place of the complicated *ab initio* electrostatic potential for molecules. We have calculated the field ionization probability and the Keldysh adiabatic parameter γ for O_2, N_2, SO_2, C_2H_4, CH_3CN and C_6H_6 in an intense laser field using the modified Coulomb potential. The results agree excellently with those derived from the *ab initio* electrostatic potential. Considering the difficulty of calculating the accurate *ab initio* electrostatic potential of molecules, our semi-empirical model provides a simple way to treat the field ionization of molecules. Moreover, as the modified parameter P of the modified Coulomb potential can be found from experimental results, the field ionization mechanism of molecules can be easily predicted using our new model.

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