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The multielectron dissociative ionization dynamics of N_2 molecule in intense femtosecond laser fields with arbitrary polarization*

Chen Jian-Xin(陈建新) and Gong Qi-Huang(龚旗煌)†

State Key Laboratory for Mesoscopic Physics, Department of Physics, Peking University, Beijing 100871, *China*

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The field-ionization Coulomb explosion model is extended to investigate the multielectron dissociative ionization process of N_2 molecule irradiated by an intense femtosecond laser field with an arbitrary polarization. The ionization process of N_2 molecule is found to be optimal at the critical internuclear distance R_c=7a.u., which is independent of the laser polarization state, the molecular explosion channel and the angle between the molecular axis and the direction of laser electric field. The kinetic energies of the ion fragments are identical in the cases of linear and circular polarizations at the same incident laser intensity. However, the probability of electron ionization is very sensitive to the above three parameters. At the critical distance R_c=7a.u. the angular dependence of the threshold intensity for the over-the-barrier ionization leads to the geometric alignment of molecules in the case of linear polarization. The threshold intensity in the case of circular polarization is apparently higher than that in the case of linear polarization, which can well explain the significant decrease of ionization in the case of circular polarization. The numerical calculations are compared with the experimental measurements.

Keywords: multielectron dissociative ionization, arbitrary femtosecond laser polarization, N_2
PACC: 3380, 3190, 4260H

The multielectron dissociative ionization of diatomic molecules in intense femtosecond laser fields has been studied in the last decades. Many experiments performed with diatomic molecules such as N_2, O_2, Cl_2 and I_2 have indicated that the ratios of the measured kinetic energies to Coulomb repulsion energy at an equilibrium internuclear distance are approximately 47% for N_2, 42% for O_2, 70% for Cl_2 and 75% for I_2.[1−4] This is valid for all measured explosion channels, and does not depend much on the laser wavelength and pulse duration. Several theoretical models have been developed to interpret this loss of Coulomb repulsion energy using the concepts of critical internuclear separation,[5−9] charge resonance effect[10−12] and screening effect of escaping fragments.[13,14] The field ionization Coulomb explosion model considers that a single outer electron is bounded by the double-well potential of a diatomic molecule in the laser electric field. It can be used to calculate the minimum laser intensity, which is required for the over-the-barrier ionization, as a function of the internuclear distance. The critical internuclear separation R_c is defined as a spacing where the ionization threshold intensity is lowest.[5−8] The model based on a full quantum approach also gave the internuclear distance that maximized the ionization rate.[9] Although these two methods are quite different, they have all successfully concluded that the molecular Coulomb explosion occurs at a larger internuclear separation than the equilibrium distance. In simulating the ionization rate of H_2^+ by numerically solving the three-dimensional time-dependent Schrödinger equation, the enhanced ionization of molecules in an intense laser field was explained as the results of charge resonance effects, and the two-step Coulomb explosion model was established.[10−12] The Thomas-Fermi model suggested that the reduction of kinetic energies could be explained in terms of a screening effect of

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†E-mail: qhgong@pku.edu.cn

escaping fragments by the ejected-electron.[13,14]

In above theoretical models and experiments, only the linearly polarized laser was considered. Recently the elliptically polarized light, particularly the circularly polarized light has been experimentally used to study the molecular Coulomb explosion in intense femtosecond laser fields. Cornaggia *et al* have found that the molecular relaxation does not depend on the angle between the molecular axis and the direction of laser electric field.[15] The identical kinetic energies of the ion fragments was measured in the cases of linear and circular polarizations. However, the significant decrease of ionization in the case of circular polarization was found in experiments.[15−20]

In this paper, the field ionization Coulomb explosion model is extended to the case of femtosecond laser field with an arbitrary polarization and the dissociation dynamics of N_2 is investigated. The critical internuclear distance R_c where molecular Coulomb explosion occurs and the significant decrease of ionization in the case of circular polarization are discussed. The numerical calculations are compared with the experimental observations.

According to the field-ionization Coulomb explosion model,[5−8] the multielectron dissociative ionization (MEDI) of diatomic molecules in intense femtosecond laser fields might be understood in the following way. When a molecule is ionized beyond the single-ion stage, the ion fragments mutually repel in the Coulomb field. The molecule starts to be dissociated. If additional electrons are stripped away in the course of the molecular dissociation, the ion fragments are subjected to an additional Coulomb repulsion and thereby gain energy. Here we consider the molecule irradiated with an arbitrarily polarized laser. The outer electron in the molecule is assumed to move freely in the double-well potential of the two ion cores. The two-dimensional double-well potential in an arbitrary laser polarization can be modelled by

$$\begin{aligned} U(x,y)(\mathrm{eV}) = &-\frac{13.6Q}{\sqrt{(x+R/2)^2+y^2}} \\ &-\frac{13.6Q}{\sqrt{(x-R/2)^2+y^2}} \\ &-1.46\times10^{-7}x\cos(\theta)\sqrt{\frac{I}{1+\varepsilon^2}} \\ &-1.46\times10^{-7}y\sin(\theta)\sqrt{\frac{I}{1+\varepsilon^2}}, \end{aligned}$$

where $Q = Q_1 + Q_2$ is the sum of the two atomic core charges. R (a.u.) is the molecular internuclear separation. The two atomic cores are assumed to be located at $(\pm R/2, 0)$. I (W/cm^2) is the incident laser intensity. ε represents the extents of elliptical polarization with $\varepsilon = 0$ and $\varepsilon = 1$ corresponding to linearly and circularly polarized lasers, respectively. θ refers to the angle between the molecular axis and laser polarization direction. Figure 1(a) shows the two-dimensional double-well potential for N_2 when the $\theta = 45°$, R=7a.u., $\varepsilon = 1$, $I = 1.11\times10^{14}$W/cm^2 and $Q_1 = Q_2 = 1$ are chosen. Figure 1(b) shows that the contour of this double-well potential can clearly present the locations of the two saddle points in Fig.1(a).

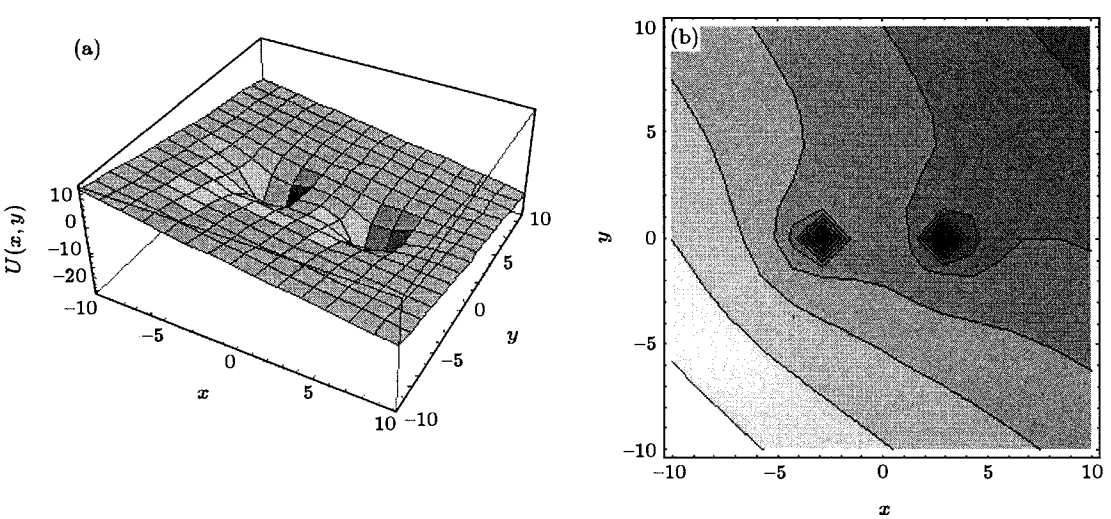


Fig.1. (a) The two-dimensional double-well potential for N_2 when the $\theta = 45°$, R=7a.u., $\varepsilon = 1$, $I = 1.11\times10^{14}$W/cm^2 and $Q_1 = Q_2 = 1$ are chosen. (b) The contour of the double-well potential of (a).

During the following calculation, the positions of the two saddle points can be obtained by finding the points where

$$\frac{\partial U(x,y)}{\partial x} = \frac{\partial U(x,y)}{\partial y} = 0.$$

The outer electron energy in this double- well potential can be approximated by[7]

$$E(\mathrm{eV}) = \frac{(-E_1 - 27.2Q_2/R) + (-E_2 - 27.2Q_1/R)}{2}.$$

To escape from the double-well potential, the outer electron in the molecule must have enough energy to pass one of the saddle points of the inner and outer potential barriers. On the other hand, the inner barrier will localize the electron for the electron energy level is lower than the inner barrier. The electron localization and Stark-Shift must be considered in this case. So there exist three cases for the electron passing the double-well potential. The first case is that the electron energy level reaches the outer potential when the inner barrier is lower than the outer barrier and the electron energy level. The second case is that the electron energy level, which is Stark-Shifted upwards by an amount $\Delta E = \dfrac{1.46 \times 10^{-7} R\cos(\theta)}{2}$, touches the outer potential as the electron energy level is between the inner barrier and the outer barrier. The last case is that the Stark-Shifted electron energy level touches the inner barrier while the inner barrier is higher than the outer barrier and electron energy level. Using a classical over-the-barrier approach, we can calculate the threshold intensity, which is required for over-the-barrier ionization, as a function of the internuclear distance R for ion fragments coming from the different explosion channels, elliptically polarized laser intensity, and angle between the molecular axis and the direction of laser electric field.

In the case of circular or elliptical polarization, the angle θ varies quickly from 0° to 360° in the course of an optical period because of the laser field rotation. The rotating angular velocity is $\omega = \dfrac{2\pi}{\lambda}$, where λ is the wavelength of the femtosecond laser. The direction of the outer electron motion changes continuously before it passes one of the saddle points of the inner and outer potential barriers. But the double-well potential can be assumed to be a constant at the instant when the outer electron passes the saddle points. So the angle θ is an important parameter for an arbitrary laser polarization state. We start with considering the simplest case where the molecular axis is parallel to the direction of laser polarization. The angle θ is zero in this case. Figure 2 shows the threshold intensity, which is required for over-the-barrier ionization, as a function of the internuclear distance R when ion fragments originate from explosion channel (1,1) in a series of elliptical polarization laser fields. For all values of the internuclear distance R, the threshold intensities have a minimum value for $\varepsilon = 0$ and a maximum value for $\varepsilon = 1$. However, the critical distance R_c, where the ionization threshold intensity is lowest, is the same (R_c=7a.u.) as that in an arbitrary laser polarization state. This indicates that the critical distance R_c is independent of laser polarization state when the molecular axis is parallel to the direction of laser electric field. Then we check whether this critical distance R_c is kept constant when the angle θ is not zero. Figures 3 and 4 present the threshold intensity as a function of the internuclear distance R for a series of angles in the cases of linear and circular polarizations, respectively. The obtained trend is very

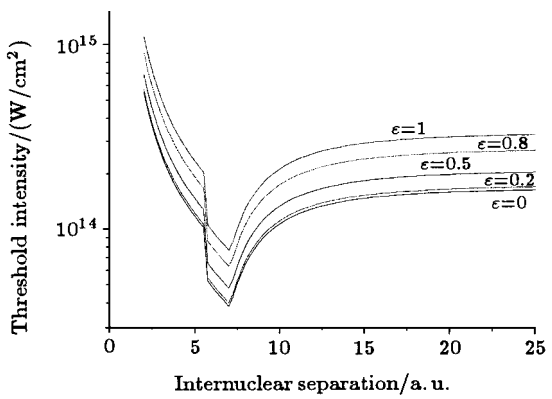


Fig.2. The threshold intensity, which is required for over-the-barrier ionization, as a function of the internuclear distance R when ion fragments originate from the explosion channel (1,1) in a series of elliptically polarized laser fields.

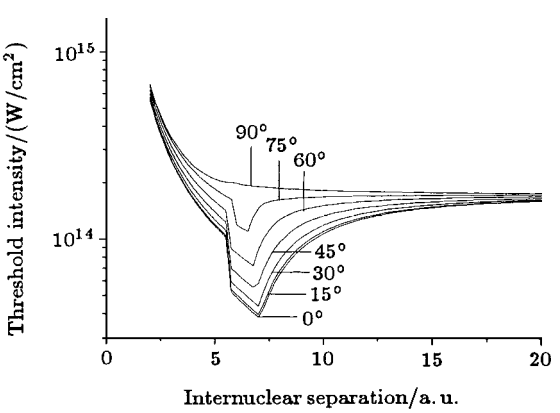


Fig.3. The threshold intensity as a function of the internuclear distance R for a series of angles in the case of linear polarization.

similar in the two cases. The threshold intensities increase with the increase of angle θ at each value of the internuclear distance R. The critical distance R_c remains unchanged for different angles, which is nearly equal to that for angle $\theta = 0°$.

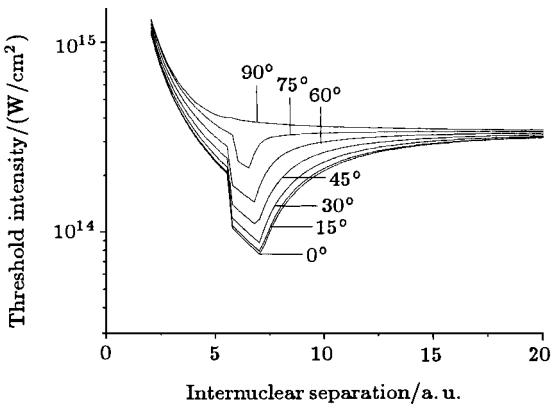


Fig.4. The threshold intensities as a function of the internuclear distance R for a series of angles in the case of circular polarization.

According to Figs.2–4, we conclude that the critical distance R_c is not dependent on the direction of the internuclear axis relative to the laser electric field and remains unchangeable in the cases of linear polarization and circular polarization. At last, we consider the different explosion channels. The angle $\theta = 0°$ is selected. Figures 5 and 6 show the threshold intensity as a function of the internuclear distance for different explosion channels (Q_1, Q_2) of N_2 in the cases of linear and circular polarizations, respectively. It is noted that the critical internuclear distances R_c for all channels have nearly the same value. The results suggest that the critical distance R_c is also independent of different explosion channels in the case of either linear or circular polarization. It is well known that the critical

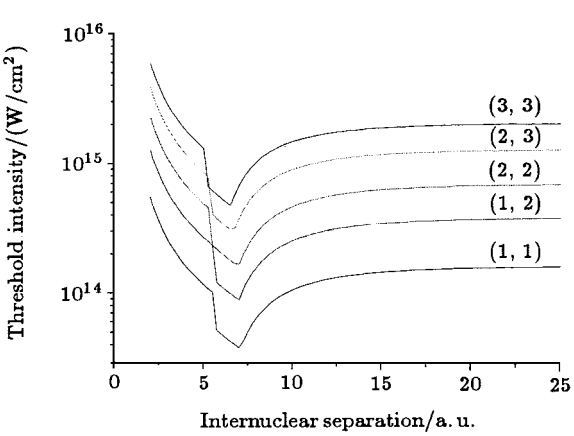


Fig.5. The threshold intensity as a function of the internuclear distance R for different explosion channels (Q_1, Q_2) of N_2 in the case of linear polarization.

distance R_c determines the kinetic energies of the ion fragments. From Figs.2–6, we conclude that the observed kinetic energies of the ion fragments arising from the same channel will be identical in the cases of linear and circular polarizations at the same incident laser intensity.

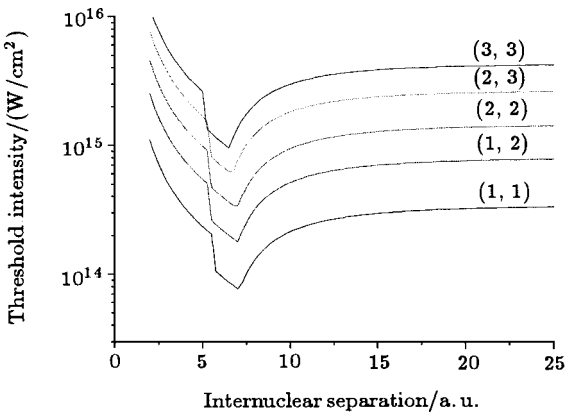


Fig.6. The threshold intensity as a function of the internuclear distance R for different explosion channels (Q_1, Q_2) of N_2 in the case of circular polarization.

The above conclusion can be verified experimentally by means of time-of-flight mass spectrometry. A flat disc with a small hole at the centre is inserted along the time-of-flight mass spectrometer axis. In the cases of linear and circular polarizations, only ion fragments coming from the molecules with the internuclear axes being along the spectrometer axis can pass through the small hole and can be observed. Cornaggia *et al* have performed this experiment for N_2.[15] A 1-mm diameter hole was used in their experiment. The experimental data show that the covariance map of N_2 with circular laser polarization looks like that with linear laser polarization. Measured kinetic energies of ion fragments coming from different explosion channels from the N_2 molecules in these two cases are identical. They also investigated the kinetic energies of ion fragments as a function of the angle θ between the linear laser polarization direction and the spectrometer axis when the incident laser intensity of $I = 3.5 \times 10^{15}\mathrm{W/cm^2}$ is kept unchanged. Their overall results show that the molecular relaxation is not dependent on the position of the laser electric field relative to the molecular internuclear axis. The experimental results are in good agreement with our calculation.

In some experiments,[15,16] a flat disc with a small hole at the centre is usually replaced by a high transmission grid for collecting all the ions. In this case, the angle θ between the molecular internuclear axis

and laser field direction must be considered. It is well known that the time-of-flight difference $T(\boldsymbol{P})-T(\boldsymbol{P}=0)$ of an ion with an initial momentum $\boldsymbol{P}$ observed in experiments is used to calculate kinetic energy of the ion. It is closely related to the projection $P(\cos(\theta))$ of $\boldsymbol{P}$ along the spectrometer axis. $T(\boldsymbol{P}) - T(\boldsymbol{P}=0) = P\cos(\theta)/ZeF_{\rm c}$, where Z is the ion charge state, e is the elementary charge and $F_{\rm c}$ is the extract electric field. In the experiment performed by Cornaggia *et al*, although the ion distribution depends on the modulus P of the vector momentum $\boldsymbol{P}$ due to the initial isotropic emission of ion fragments in the case of circular polarization, the N^{m+}/N^{n+} $(m, n$=2,3) covariance islands become straight lines with constant $C_2(T_1,\ T_2)$ values. The slopes are n/m because the $\boldsymbol{P}_n + \boldsymbol{P}_m$=0 momentum conservation is equivalent to $mT(N^{m+})+nT(N^{n+})$=constant.[15] If this effect were not considered, the measured kinetic energies in the case of circular polarization would be lower than that in the case of linear polarization.[16]

Although the kinetic energies of ion fragments does not depend on the laser polarization state, the electron ionization is very sensitive to it (as shown in Figs.2–6). At the critical distance, the threshold intensity that is required for over-the-barrier ionization in the case of circular polarization is always higher than that in the case of linear polarization. Figure 7 presents the threshold intensity as a function of the laser polarization state at the critical distance for different explosion channels of N_2 molecule. The angle $\theta = 0^\circ$ is selected.

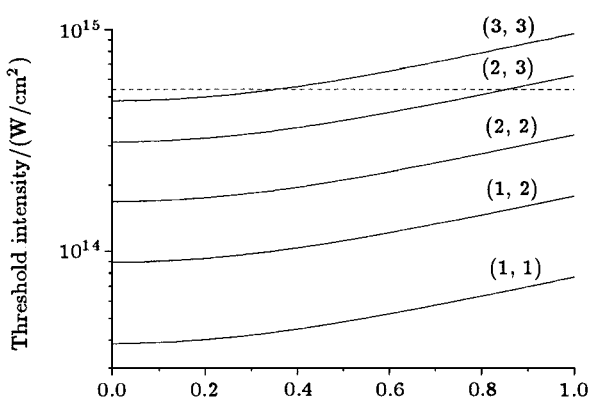


Fig.7. The threshold intensity as a function of the laser polarization state at the critical distance for different explosion channels of N_2 molecule.

If the incident laser intensity of 4×10^{15}W/cm^2 is used (denoted by a the horizontal broken line), the explosion channel (2,3) can not make contribution to the yields of N^{2+} and N^{3+} ions for $\varepsilon = 1$. When the angle θ is changeable, the laser polarization state could suppress other channels. This can well explain the significant decrease of ionization in the case of circular polarization.[15–20] But this result is different from the experimental data of Talebpour's group.[21] They reported that the fragmentation pattern of molecules was not affected by the laser polarization and relative ratios of ion yields were essentially similar in the cases of linear and circular polarizations. In the case of linear polarization, the threshold intensity that is required for over-the-barrier rises with the increase of angle θ (as shown in Fig.3). At the critical distance $R_{\rm c}$, this angular dependence is strongest, which will result in the geometric alignment of molecules.

A field-ionization Coulomb explosion model has been developed, which is valid for the laser field with an arbitrary polarization. The multielectron dissociative ionization dynamics of N_2 in intense femtosecond laser fields with arbitrary polarizations have been investigated using this model. The calculations show that the critical distance $R_{\rm c}$ where molecular Coulomb explosion takes place does not depend on the laser polarization state, the molecular explosion channel and the angle between the molecular internuclear axis and the direction of laser electric field. However the probability of electron ionization is very sensitive to them. The conclusions about ion fragments with identical kinetic energies in the laser field with an arbitrary polarization and the significant decrease of ionization in the case of circular polarization are compared with the experimental observations.

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