

## Effects of orbital symmetries on the ionization rates of aligned molecules by short intense laser pulses

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It is shown that by measuring the angular distributions of fragmented ions of simple molecules by sub-10 fs laser pulses at intensities in the non-sequential double ionization regime the electron density of the highest occupied molecular orbital can be probed directly. For pulses of a few tens of femtoseconds or longer, it is shown that the angular distributions of the ions are dominated by post-ionization alignment which results from the additional rotation of the molecular axis during the breakup process. These models are used to explain recent experiments.

### 1. Introduction

When neutral molecules are subjected to intense infrared laser pulses of sufficiently high intensity, they undergo single or multiple ionization followed by immediate dissociation. Many experiments have shown that the ionized products are strongly forward peaked in the direction of the laser polarization. The nature and the mechanism for resulting in such strong anisotropic angular distributions of the final ion fragments, however, is a subject of debate since the 1990s. Specifically it is known for a long time that neutral molecules can be dynamically or adiabatically aligned before ionization by the laser [1]. Furthermore the ionization rates of molecules by lasers are expected to depend on the orientation and alignment of molecules. For laser pulses of durations in the order of tens of femtoseconds, the alignment effect for heavy molecules such as  $I_2$  is expected to be small. For light molecules both mechanisms may be important and the method for disentanglement of one from the other is not apparent. Until recently most studies of dissociative ionization in diatomic molecules reported angular distributions of ion fragments in a narrow angular cone around the laser polarization direction [2–4]. But in a series of papers recently from Kansas State University [5–8] the dissociative ionization of diatomic and simple polyatomic molecules has been studied for laser pulses as short as 8 fs, and distinct angular distributions of fragment ions away from the

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laser polarization direction have been found. In fact, for molecules like O<sub>2</sub> and CO<sub>2</sub>, for example, the angular distributions in the polarization direction for 8–10 fs pulses were actually found to have minima.

In this paper we address the fragmentation dynamics of molecules in the laser fields. Starting with an ensemble of isotropically distributed molecules, we (i) first calculated the time evolution of the alignment of molecules induced by the linearly polarized light, (ii) included the alignment dependent ionization rates using the molecular tunneling ionization model (MO-ADK) of Tong *et al.* [9], (iii) accounted for the further alignment toward the polarization axis during the breakup process. The last effect, which we called post-ionization alignment (PIA), has been addressed and estimated previously using classical theory [10]. Recently, we have developed a full quantum theory to describe the PIA effect [7]. Only after all the three effects are properly accounted for can one compare the resulting theoretical angular distributions of the ions with experimental measurements.

The rest of this paper is arranged as follows. In section 2 we discuss the alignment of molecules in the laser field, the MO-ADK model and then the theory for PIA. In section 3 the experimental angular distributions of the fragmented ions of molecules by sub-10 fs pulses where alignment of molecules by lasers and the PIA effect are not important, are compared with the predictions of the MO-ADK theory and with the shape of the outermost occupied molecular orbitals. We show that the angular distributions of the ions mimic the geometric shape of the electron density of the highest occupied molecular orbitals of the target directly. In section 4 the breakup of molecules by laser pulses of duration of tens of femtoseconds are shown to peak toward the laser polarization direction due to the PIA effect. The last section gives a short summary.

## 2. Theory of angular distributions of molecule breakup in a laser field

### 2.1 Molecular tunneling ionization theory

Since the electronic charge density in a molecule is not isotropic it is clear that the ionization rates of molecules in an intense laser field will depend on the alignment of molecules with respect to the laser polarization direction. For many years such alignment dependence could not be readily evaluated until the molecular tunneling ionization theory (MO-ADK) [9] was developed. The tunneling ionization theory for atoms has been in existence for many years. In the version for ionization by laser fields, in the so-called ADK (Ammosov-Delone-Krainov) model [11] the ionization rate is given analytically. The MO-ADK theory for the ionization of molecules is also given analytically. It further predicts simple alignment dependence of the ionization rates. Here we briefly summarize this model.

For an atom, the wavefunction of the valence electron at a large distance where tunneling occurs can be written as

$$\Psi^m(\mathbf{r}) = C_\ell F_\ell(r) Y_{\ell m}(\hat{\mathbf{r}}), \quad (1)$$

where

$$F_\ell(r \rightarrow \infty) \approx r^{Z_c/\kappa-1} e^{-\kappa r}, \quad (2)$$

with  $Z_c$  being the effective Coulomb charge,  $\kappa = \sqrt{2 * I_p}$ , and  $I_p$  the ionization energy. These expressions are for an electron with angular momentum quantum numbers  $\ell$  and  $m$ . For molecules, the electronic wavefunction is multi-center in nature. To employ the ADK formula directly, one needs to expand the wavefunction in the asymptotic region in terms of one-center expressions. Thus one writes the molecular wavefunction in the tunneling region as

$$\Psi^m(\mathbf{r}) = \sum_{\ell} C_{\ell} F_{\ell}(r) Y_{\ell m}(\hat{\mathbf{r}}), \quad (3)$$

where the summation over  $\ell$  is needed. The coefficients  $C_{\ell}$  are obtained by fitting the asymptotic molecular wavefunction. They depend on the internuclear separation and on the electronic state. Once the coefficients  $C_{\ell}$  are available the ionization rate for a diatomic molecule with its axis aligned with the laser polarization is given by

$$w_{\text{stat}}(F, 0) = \frac{B^2(m)}{2^{|m|} |m|! \kappa^{2Z_c/\kappa-1}} \left( \frac{2\kappa^3}{F} \right)^{2Z_c/\kappa-|m|-1} e^{-2\kappa^3/3F}, \quad (4)$$

where

$$B(m) = \sum_{\ell} C_{\ell} Q(\ell, m), \quad (5)$$

and

$$Q(\ell, m) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell+|m|)!}{2(\ell-|m|)!}}. \quad (6)$$

Clearly the factor  $B^2(m)$  measures the electron density in the tunneling region along the direction of the electric field. If the molecular axis is not aligned along the field direction, but at an arbitrary angle  $\mathbf{R}$  with respect to the field direction, the  $B(m)$  in equation (4) is expressed as

$$B(m') = \sum_{\ell} C_{\ell} D_{m',m}^{\ell}(\mathbf{R}) Q(\ell, m'), \quad (7)$$

with  $D_{m',m}^{\ell}(\mathbf{R})$  being the rotation matrix and  $\mathbf{R}$  the Euler angles between the molecular axis and the field direction. The static field ionization rate is

$$w_{\text{stat}}(F, \mathbf{R}) = \sum_{m'} \frac{B^2(m')}{2^{|m'|} |m'|! \kappa^{2Z_c/\kappa-1}} \left( \frac{2\kappa^3}{F} \right)^{2Z_c/\kappa-|m'|-1} e^{-2\kappa^3/3F}. \quad (8)$$

The ionization rate in a low frequency laser field is given by

$$w(F, \mathbf{R}) = \left( \frac{3F}{\pi\kappa^3} \right)^{1/2} w_{\text{stat}}(F, \mathbf{R}). \quad (9)$$

where  $F$  is the peak field strength.

An immediate consequence of the MO-ADK theory is that the ionization rates for any space-fixed molecules are proportional to the electron density in the direction of the laser polarization direction. In other words, by measuring the alignment dependence of the ionization rates, the electron density of the outermost molecular orbital can be directly probed. This is the most significant prediction of the MO-ADK theory.

We comment that there is a number of other theories for the ionization of molecules by lasers in recent years [12, 13]. Still for the purpose of this paper we will focus only on the MO-ADK theory for its simplicity and for its transparent predictions on the symmetry properties of the molecular wavefunctions.

## 2.2 Alignment of molecules by lasers

When a homonuclear diatomic molecule is placed in a laser field, due to the anisotropic dipole polarizability, each molecule will receive a torque from the laser field. By treating the diatomic molecule as a rigid rotor [14–17], the rotational motion of a homonuclear molecule with initial state  $\Phi_{JM}(\theta, \phi, -\infty) = Y_{JM}(\theta, \phi)$  evolves in the laser field following the time-dependent Schrödinger equation (in atomic units  $m = \hbar = e = 1$ ),

$$i \frac{\partial}{\partial t} \Phi_{JM}(\theta, \phi, t) = \left[ B \hat{J}^2 + \frac{1}{2} \vec{F}(t) \cdot \vec{\alpha} \cdot \vec{F}(t) \right] \Phi_{JM}(\theta, \phi, t). \quad (10)$$

Here  $B$  is the rotational constant,  $\vec{\alpha}$  is the polarizability (tensor), and  $\vec{F}(t)$  is the time dependent laser field. The above equation can be solved using the split-operator-method in the energy representation [18]. The time-dependent alignment distribution can be obtained as

$$\rho(\theta, t) = \sum_{JM} \omega_{JM} |\Phi_{JM}(\theta, \phi, t)|^2, \quad (11)$$

where  $\omega_{JM}$  is the weight according to the Boltzmann distribution. For homonuclear molecules, nuclear spin statistics has to be properly accounted for as well. For diatomic molecules in a linearly polarized laser field, the angular distribution, or the alignment, does not depend on the azimuthal angle  $\phi$ . The two equations above allow the determination of the time dependence of the angular distributions of homonuclear diatomic molecules in a laser field. They describe the dynamic alignment of molecules in the laser field, as well as the rotational revival of the enhanced alignment after the laser field has been turned off. The model assumes that the molecules remain in the ground state at the equilibrium position and that no ionization happens.

## 2.3 Post-ionization alignment of molecules in an intense laser pulse

In the previous subsection the alignment of molecules in the laser field was derived under the assumption that the vibrational and the electronic degrees of freedom are not excited, i.e., dissociation or ionization do not occur. To probe the alignment, or the anisotropic angular distributions of molecules, Coulomb explosion techniques

are often used. The neutral molecules are ionized with short intense laser pulses and the angular distributions of the fragmented ions are determined. Since the Coulomb explosion energy is large, it was often assumed that the fragmentation process is “instantaneous” that the direction of the two fragmented ions is the direction of the molecule before ionization. However, a simple estimate shows that this is not the case for light molecules for laser pulses of duration of tens of femtoseconds that are typically used in such experiments.

Consider a Gaussian laser pulse with pulse duration  $\tau$  (FWHM). We can calculate classically the angular momentum received by each molecule from the laser pulse,

$$L = \frac{1}{2}(\alpha_{\parallel} - \alpha_{\perp}) \sin(2\theta_0) \int_{-\infty}^{\infty} F^2(t) dt = \sqrt{\frac{\pi}{\ln 2}} \frac{I\tau}{8} (\alpha_{\parallel} - \alpha_{\perp}) \sin(2\theta_0). \quad (12)$$

where  $\theta_0$  is the initial angle of the molecule. Suppose at  $t=0$  (at the peak of the laser intensity) the molecule is first ionized and that we neglect the time interval between the first and the second ionizations. Take  $\text{O}_2$  as the example. The  $\text{O}_2^{2+}$  ion starts the breakup at  $t=0$ . Due to the initial rotational angular momentum of the molecule at the time of the second ionization, the axis between the two ions will rotate an additional angle until they are well separated. This angle is easily integrated to be

$$\delta\theta = \int_0^{\infty} \omega dt = \int_{R_0}^{\infty} \omega \frac{dR}{v(R)} = L \sqrt{\frac{2}{R_0\mu}}. \quad (13)$$

In deriving the above equation, we have used the following relations:

$$L = \mu R^2 \omega, \quad (14)$$

$$v(R) = \frac{dR}{dt} = \sqrt{\left[ \frac{2}{\mu} (V(R_0) - V(R)) \right]}, \quad (15)$$

where  $\mu$  is the reduced mass,  $R_0$  is the equilibrium distance and  $V(R)$  is the potential curve of the  $\text{O}_2^{2+}$ , which was approximated by  $V(R) = 1/R$ . For  $\text{O}_2$  molecules, we get  $\delta\theta = 0.066 I\tau \sin(2\theta)$  in degrees. Here,  $I$  is the laser peak intensity in units of  $I_0 = 10^{14} \text{ W/cm}^2$ , and  $\tau$  is laser pulse duration in fs. Note that we will use  $I_0$  as the unit of laser intensity since we are interested in the laser intensity in the order of  $I_0$ . Based on this simple classical model, the PIA effect will rotate the axis between the two ions by about 5 degrees for a 35 fs laser pulse at  $2.2 I_0$ . Note that this classical PIA is the consequence of the breakup of a rotating linear molecule. It is not very sensitive to whether the laser fields are present or not during the breakup process.

We can incorporate a quantum mechanical analysis of the PIA effect following the standard treatment of the rotational motion of a homonuclear molecule in a laser field as in the previous subsection. To incorporate the post-ionization alignment effect into the formulation, we assume that the doubly charged molecular ions are created at  $t=0$  and  $R = R_0$  where the Coulomb explosion gets started. As the doubly charged molecular ion breaks, the dipole polarizability changes

with  $R$ , and the velocity of the atomic ions relative to each other increases, following equation (15). In the meanwhile, the moment of inertia of the “rigid rotor”  $O_2^{2+}$  increases quadratically with  $R$ . The time-dependence of  $B$  and the dipole polarizability  $\bar{\alpha}$  can be entered into the time-dependent equation (10) through their variations with  $R(t)$ . Note that equation (10) still exhibits nontrivial time-dependence even after the laser has been turned off. [This was used in the classical estimates, equations (12) and (13).] The time-dependent equations are integrated until the two atomic ions are far apart at which time the angular distributions of the ion fragments are calculated. The “realistic” dipole polarizability as a function of the internuclear separation has been calculated by an *ab initio* quantum chemistry code (GAMESS) [19].

### 3. Alignment dependence of tunneling ionization rates and the symmetry of molecular orbitals

According to the MO-ADK theory discussed in section 2, the alignment dependence of the tunneling ionization rates is a direct measure of the electron density of the highest occupied molecular orbital (HOMO) if the molecules are isotropically distributed initially. To measure the orientation of the molecule, or more precisely, the direction of the molecule at the time of ionization, it is most convenient if the ionized molecules break up into two fragmented ions, where the events are clearly identified when their momenta are summed to zero. Such experiments are routinely employed in experiments using COLTRIMS apparatus [20, 21] where the momentum of individual fragmented ions is measured over  $4\pi$  angles.

In order to extract the alignment-dependent ionization rates of molecules from such experiments, additional conditions must be met. First, the laser pulses should not align the molecules, either before or after the ionization. Next, the second ionization of the molecules should be mostly isotropic, i.e., independent of the alignment of the molecules. These two conditions are met using sub-10 fs laser pulses at low intensities in the so-called non-sequential double ionization region. In such process, the first electron is ionized near the peak of the laser pulse. The released electron is driven back about three quarters of an optical cycle later to recollide with the molecular ion to excite it or to ionize it. If it is excited, the molecular ion will be ionized a quarter optical cycle later when the laser reaches the peak field again. Since the second ionization is due to the impact from the returning electron, this process is less sensitive to the alignment of molecules. Thus we will assume that the second ionization is isotropic which is consistent with the COLTRIMS results for  $H_2$  molecules [22, 23].

Under these assumptions, we compare in figure 1 the angular distributions of the measured fragments for a number of molecules taken at Kansas State University [5–8]. Shown are the results for  $N_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$  and  $C_2H_2$ . For  $CO_2$ , the breakup channel considered was  $CO_2^{2+} \rightarrow CO^+ + O^+$  and for  $C_2H_2^{2+}$  into two  $CH^+$  ions. These distributions are compared with the alignment-dependent ionization rates of molecules using the MO-ADK theory (2nd column) and with the

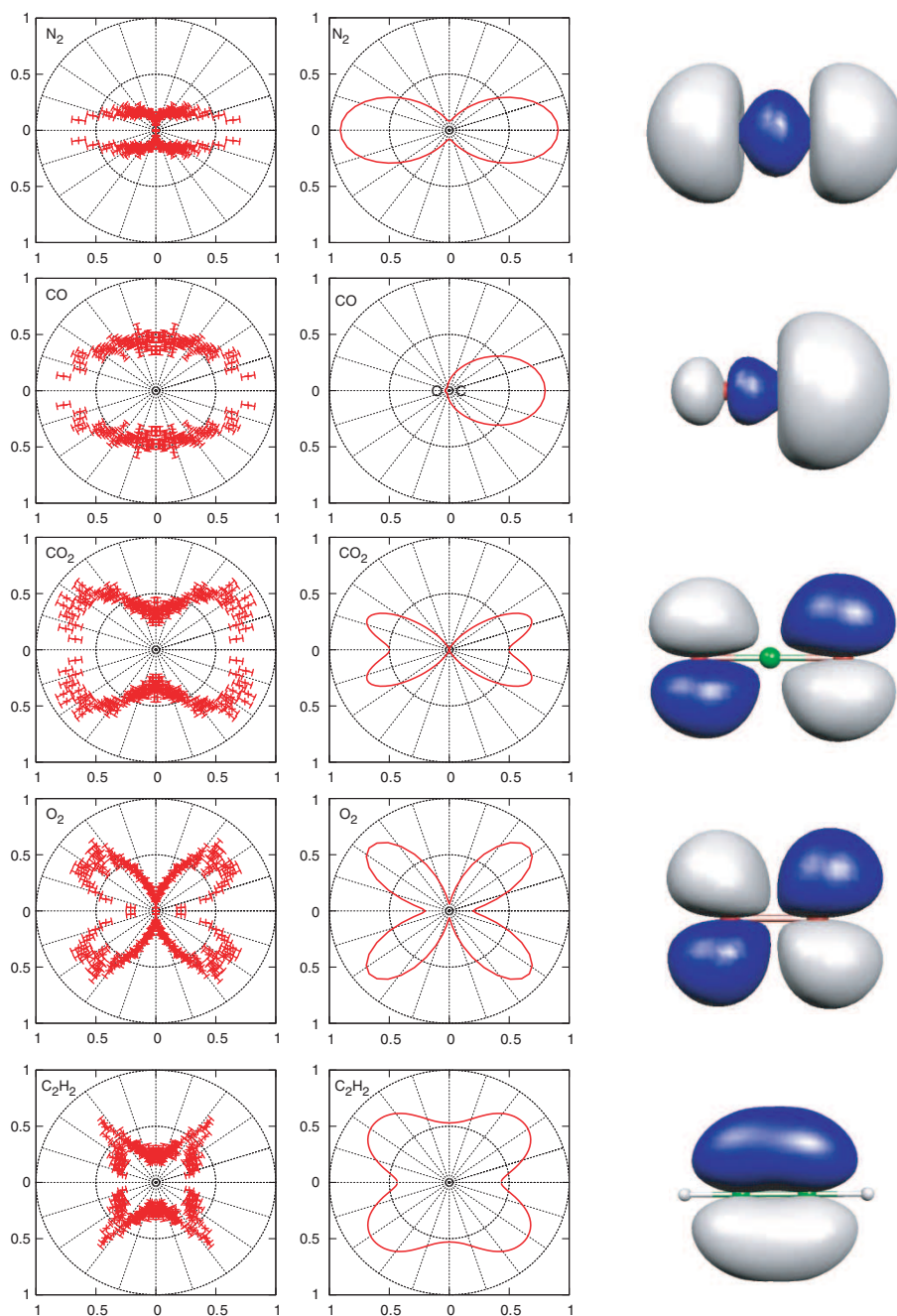


Figure 1. Comparison of the measured angular distributions of the fragmentation (first column) with the simulated angular distributions of the first ionization (second column) for  $N_2$ , CO,  $CO_2$ ,  $O_2$  and  $C_2H_2$ , respectively. The corresponding molecular orbitals are also plotted (third column). The experimental data are taken from references [5, 6, 8]. (The colour version of this figure is included in the online version of the journal.)

density distributions of the molecular orbitals (3rd column) from which the electrons have been ionized, calculated from the GAMESS code at the equilibrium distance for each molecule. The calculated electronic wavefunction is visualized by the MOLEKEL program [24].

In figure 1 the angular distributions for  $\text{N}_2$  and  $\text{CO}$  are quite similar. The HOMO of  $\text{N}_2$  has  $\sigma_g$  symmetry and of  $\text{CO}$  has  $\sigma$  symmetry and their angular distributions are peaked in the direction of the laser polarization, in agreement with the fact that the electron density for  $\sigma_g$  (or  $\sigma$ ) orbitals peaks in the direction of the internuclear axis. (The experiments cannot separate C–O from O–C in the sample so their angular distribution is symmetric.)

In figure 1 we also note that the angular distributions for  $\text{O}_2$  and  $\text{CO}_2$  are very similar. Their angular distributions peak away from the laser polarization direction. The HOMO of each molecule has  $\pi_g$  symmetry, and according to the MO-ADK theory the ionization rate peaks when the molecules are aligned at an angle of about  $40^\circ$  for  $\text{O}_2$  and  $25^\circ$  for  $\text{CO}_2$ . The latter has a smaller angle because the O–O bond length is larger. The ionization rates show a minimum at the laser polarization direction instead of zero as would be expected for a pure  $\pi_g$  orbital, reflecting the approximate nature of the MO description of the HOMO orbital.

In figure 1 the angular distributions of  $\text{C}_2\text{H}_2$  are shown. For  $\text{C}_2\text{H}_2$ , its HOMO has the  $\pi_u$  symmetry. Again, the angular distributions measured are in good agreement with the prediction of the MO-ADK theory and with the symmetry property of the  $\pi_u$  orbital.

The results shown in figure 1 clearly indicate that the measurement of alignment dependence of tunneling ionization rates provides an experimental verification of the “physical reality” of molecular orbitals (MO). The MO is often considered as a mathematical construct. Its utility is tied closely to the validity of the shell model or the Hartree-Fock approximation for the ground state of molecules. It is granted that the results of figure 1 only provide the density distributions. However, the approximate nodal planes can be identified from the measured angular distributions such that wavefunctions can be deduced. We note that in most quantum measurements the yield is proportional to the square of the matrix of an operator taken between the initial and the final states. Thus it is often difficult to unravel from the measured angular distributions the geometric effect of the initial state and the final state separately. For tunneling ionization of molecules, ionization occurs primarily from electrons initially in the direction of the electric field. In the tunneling process the ionized electrons remain in the direction of the electric field. The measurement of the breakup of the molecular ion thus gives a direct measurement of the electron density distribution of the outermost orbital if the molecular axis does not undergo additional rotation in the breakup process. These conditions are met for non-sequential double ionization of simple molecules by sub-10 fs laser pulses.

We comment that there do exist discernable disagreement between the MO-ADK theory and experimental results. The limitation of the theory includes that we ignored the possible small contributions from inner molecular orbitals, which will make the region near the nodal surfaces less pronounced.



#### 4. Molecular breakup and post-ionization alignment

To interpret the experimental angular distributions of the fragmented ions of molecules in a longer laser pulse, we need to account for the dynamic alignment of the neutral molecules, the alignment dependent ionization rates and the post-ionization alignment effect. We will take  $O_2$  molecules as an example. Let  $R(\theta) = R_{\pi_g}(\theta)$  be the anisotropic ionization rate calculated according to the prediction of the MO-ADK theory where  $\theta$  is the angle of the molecular axis with respect to the laser polarization direction. We consider a Gaussian laser pulse with laser peak intensity at  $t=0$ . From equation (11) the angular distribution of the molecules at  $t=0$  can be calculated, assuming that the molecules are not ionized. If the molecules are ionized at  $t=0$  and if the two  $O^+$  ions just fly apart at the angle where  $O_2$  ionization occurs, then the angular distribution of the two  $O^+$  ions should be given by

$$S_0(\theta) \sim \rho(\theta, t=0)R(\theta). \quad (16)$$

If the PIA effect is included, then the theoretical prediction of the angular distribution is given by

$$S_f(\theta) \sim \rho(\theta, \infty)R(\theta), \quad (17)$$

In figure 2(a), we show the calculated angular distributions of the fragmented ions using the three models for the 35 fs pulses at the peak intensity of  $2.2 I_0$ , by comparing  $R(\theta)$ ,  $S_0(\theta)$  and  $S_f(\theta)$ . Clearly there is little dynamic alignment up to  $t=0$ . The major shift in the angular distribution toward the laser polarization direction comes from the PIA effect. At this intensity the angular distributions of the fragmented ions still resemble the “butterfly” structure seen for the 10 fs pulse shown in figure 1, except that the peaks have shifted toward the polarization axis. Comparing with the experimental data of Voss *et al.* [6] shown in figure 2(b), the experimental data show evidence for the PIA effect but are more forwardly peaked than the theoretical calculations.

In the present calculation, we assumed that the cross section in the second ionization, which is due to impact excitation or ionization of  $O_2^+$  by the rescattering electron, is isotropic. We used this model for the interpretation of short pulses shown in figure 1 and no significant discrepancy was observed. However, at the higher intensity of  $2.2 I_0$ , where the returning electrons have higher energies, the electron impact excitation and ionization cross sections could exhibit some alignment dependence. No calculations are available for such analysis at the present.

The discrepancy shown in figure 2 could also be due to the experimental uncertainty in laser intensity and of pulse length. In figure 3 we examine the intensity dependence of the PIA effect. For the 35 fs pulses, the dynamic alignment before ionization and the MO-ADK rates are not very sensitive to the laser intensity. However, the PIA effect depends strongly on the laser intensity, as shown in figure 3 for laser intensity of  $1.5 I_0$  and  $2.5 I_0$ .

As the laser intensity is further increased, the fragmented ions will all be forwardly peaked. In figure 4 we show the results of the calculations for a 35 fs pulse at the intensity of  $5.6 I_0$ . The experimental results from Voss *et al.* [6]

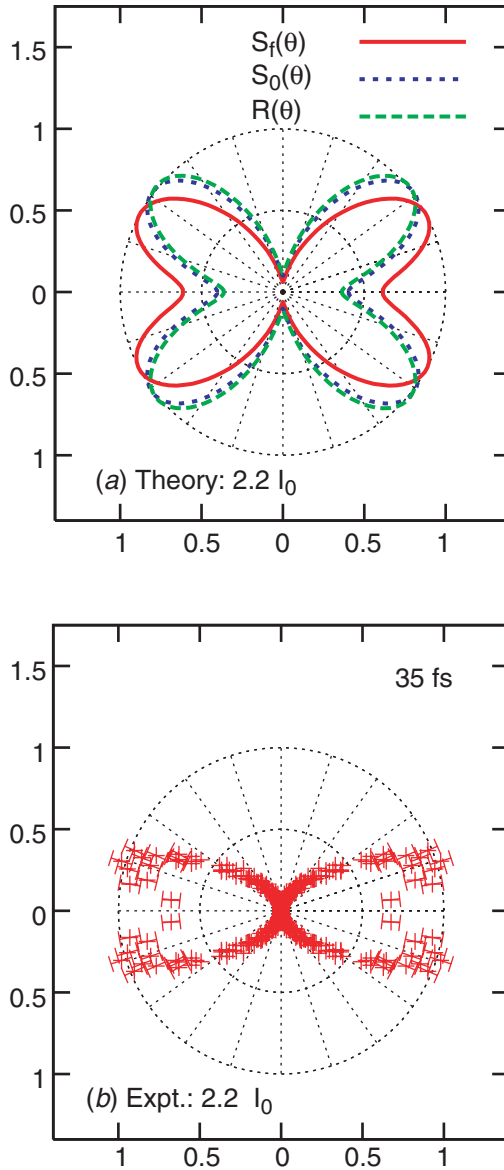


Figure 2. Comparison of the simulated angular distributions of the fragmented  $O^+$  ions for 35 fs pulsed laser fields at  $2.2 I_0$ .  $R$  is the alignment-dependent ionization rate;  $S_0$  is the angular distribution neglecting PIA, and  $S_f$  is the same distribution including PIA. (The colour version of this figure is included in the online version of the journal.)

indicate that the  $O^+$  ions are strongly forward peaked. Such strongly forward peaked angular distributions of the molecular fragments have been observed in many previous experiments. Many models have been advanced to interpret their origin. From the analysis of figure 4, it is clear that the major factor is the

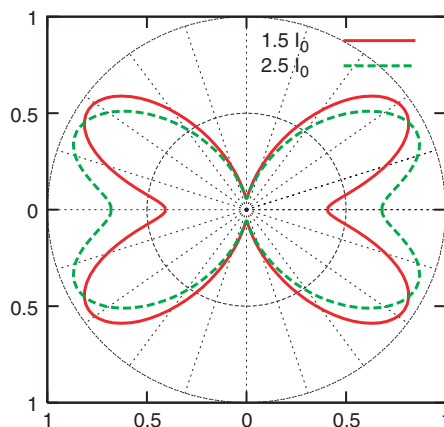


Figure 3. Angular dependent ionization signal for the breakup of  $O_2$  molecules by a 35 fs laser pulse at peak intensities of  $1.5 I_0$  and  $2.5 I_0$ , respectively. (The colour version of this figure is included in the online version of the journal.)

post-ionization alignment effect. The pulse is not long enough to align the molecules before ionization, nor the ionization rates for  $O_2$  peak in the laser direction. Even though the molecules are not aligned significantly by the laser pulses, the molecules do receive enough torque from the lasers and acquire a significant amount of angular momentum. The PIA effect reflects the additional rotation of the fragments from the breakup of such a rotating rotor.

## 5. Summary and discussion

To summarize, we show that double ionization of simple molecules by sub-10 fs laser pulses can be used to determine the electronic charge distributions of the highest occupied molecular orbitals (HOMO) directly if the laser intensity is chosen appropriately in the non-sequential double ionization regime. With short pulses at low intensity the laser field does not exert enough torque on the molecules and the molecules are not aligned by the laser field. The experimental angular distribution of the molecular ion fragments then reflects the alignment dependence of the tunneling ionization rates of molecules. The latter, according to the molecular tunneling ionization theory of Tong *et al.* [9], is directly proportional to the electron density of the molecules in the direction of the laser polarization. In other words, the method provides a direct “experimental” observation of the electronic density distribution of the HOMO. The results of figure 1 clearly illustrate such “observations” by comparing the experimental angular dependence of the fragmented ions and the molecular orbitals shown. Thus for the first time, it is possible to directly map the electron cloud distribution of a molecular orbital experimentally without the complications from the final states. For laser pulses with longer durations, e.g., even for pulses of a few tens of femtoseconds, we have shown quantitatively that the post-ionization alignment effect plays a major role in

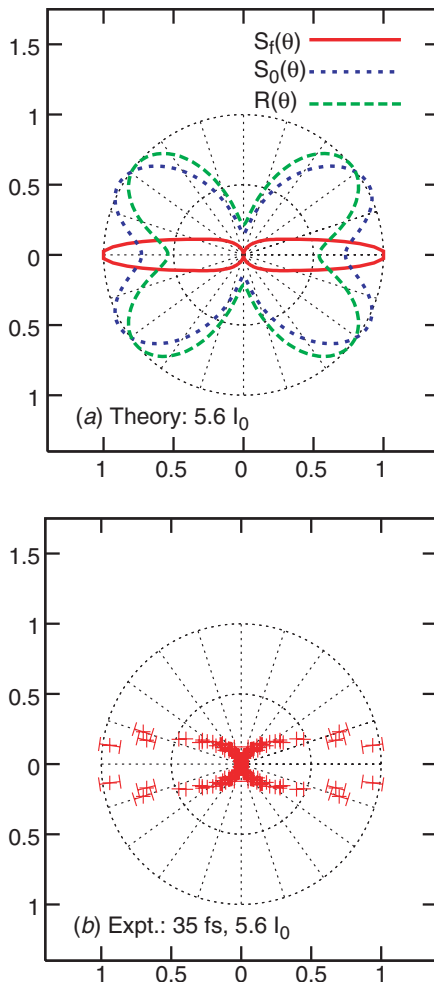


Figure 4. Comparison of the simulated angular distributions of fragmented  $O^+$  ions with the experimental data (reference [6]) by a 35 fs laser pulse at  $5.6 I_0$ .  $R$  is the alignment-dependence ionization rate;  $S_0$  is the angular distribution neglecting PIA, and  $S_f$  is the same distribution including PIA. (The colour version of this figure is included in the online version of the journal.)

determining the angular distributions of the fragmented ions. The PIA effect should be accounted for in any future interpretation of the angular distributions of the fragmentation of molecules by intense lasers.

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