

LETTER TO THE EDITOR

Dependence of strong-field photoelectron angular distributions on molecular orientation

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Abstract

We have analysed angular distributions of the photoelectron yields arising from strong-field ionization of diatomic and polyatomic linear molecules using a leading-order intense-field *S*-matrix theory. For molecules with active π electrons the distribution is found to strongly depend on the degree of molecular alignment, showing a nodal minimum along the laser polarization direction as a characteristic signature.

The nonlinear interaction of molecules with an intense laser pulse has attracted considerable experimental and theoretical interest recently (for reviews see, for example, [1, 2]). Single-electron ionization is perhaps the most fundamental process initiated during the exposure of a molecule to a strong field. A number of phenomena, e.g. charge resonant enhanced ionization of molecular ions at critical internuclear distances or the suppression of ionization of a neutral molecule to that of an atom with the same ionization potential, have been observed and analysed. Most of the experiments have been performed on ensembles of molecules with random orientation. Just recently it has become possible to measure the orientation dependence of strong-field ionization in the case of N_2 molecules [3]. The experimental observation supports theoretical predictions [4–8] that the total ionization rates of neutral diatomic molecules depend on the orientation of the molecular axis with respect to the laser field.

The dependence of ionization yields and related observables, such as photoelectron energy spectra and angular distributions, on the spatial alignment of the molecule is important for an understanding of strong-field molecular physics. For example, high harmonic yields [9, 10] and molecular dissociation yields [11–13] are influenced by the angular dependence of the ionization process. Spatial alignment of molecules is furthermore of great interest in view of the variety of possible applications [13, 14], such as control of ionization and dissociation pathways, rotational cooling, molecular trapping and focusing, pendular-state

spectroscopy and the study of steric effects in chemical reaction dynamics. It is well known from excitation–ionization experiments at low laser intensities that, in particular, photoelectron angular distributions are sensitive to molecular orientation and provide a probe of the molecular structure, symmetry and orientation (for reviews see, for example, [15, 16]). In view of the recent experimental achievements in strong-field molecular ionization the question arises as to how the highly nonlinear electron–field interaction at peak intensities well above 10^{13} W cm $^{-2}$ affects the angular distribution of the photoelectron yields depending on molecular orientation.

Below we analyse the photoelectron angular distribution of linear molecules subjected to an intense linearly polarized laser pulse. It will be shown that, for molecules having an active π orbital, the degree of alignment of the molecular ensemble is reflected in the appearance of a nodal minimum along the laser polarization direction, as the cone angle of the distribution of alignments, β , decreases from $\beta = 180^\circ$ (random orientation) to $\beta = 0^\circ$ (complete alignment along the polarization axis). The origin of the minimum lies in the presence of a symmetry-induced node in the plane containing the molecular axis.

Our analysis is carried out using an extension of the so-called KFR (Keldysh–Faisal–Reiss) theory [17–19] for atomic ionization in intense laser fields to the ionization of molecules [20–22]. It corresponds to the leading order of the *ab initio* intense-field *S*-matrix theory and involves nonresonant transitions of a molecule from the initial electronic ground state to the final state of the molecular ion and the field-dressed Volkov electron (e.g. [23]). The angular distribution of the ejected electrons, averaged over the distribution of the cone angles, can be given in terms of the rate of differential ionization per element of solid angle $d\Omega$ along the axis of electron detection, as [20, 22]

$$\frac{dW(I, \beta)}{d\Omega} = N_e 2\pi \left(\frac{(2I_p)^{3/2}}{E_0} \right)^{2Z/\sqrt{2I_p}} \sum_{N=N_0}^{\infty} k_N (U_p - N\omega)^2 \frac{1}{2\pi\beta} \int_0^{2\pi} d\phi_{\hat{n}} \int_0^\beta d\theta_{\hat{n}} \sin(\theta_{\hat{n}}) \times J_N^2 \left(\alpha_0 \cdot \mathbf{k}_N; \frac{U_p}{2\omega} \right) |\langle \phi_{k_N} \phi_f^+ | \phi_i \rangle(\hat{n})|^2 \quad (1)$$

where \hat{n} is a unit vector along the molecular axis and $\theta_{\hat{n}}$ and $\phi_{\hat{n}}$ are the angles with respect to the polarization direction $\hat{\varepsilon}$. N_e is the number of electrons in the active molecular orbital, $Z = 1$ is the charge state of the molecular ion, E_0 is the peak field strength of the laser and I_p is the ionization energy of the molecule. $J_N(a; b)$ is a generalized Bessel function of two arguments (e.g. [23]), where $\alpha_0 = \sqrt{I}/\omega$ is the quiver radius ($\alpha_0 = \alpha_0 \hat{\varepsilon}$) and $U_p = I/4\omega^2$ is the quiver energy of an electron in a linearly polarized laser field of frequency ω , intensity I and polarization direction $\hat{\varepsilon}$. ϕ_{k_N} is a plane wave and ϕ_i and ϕ_f^+ are the initial and final ground state wavefunctions of the neutral molecule and the molecular ion, which are obtained from the quantum chemical GAMESS code, within the Hartree–Fock approximation and the Born–Oppenheimer approximation [24]. $k_N^2/2 = N\omega - U_p - I_p$ is the kinetic energy of an electron on absorption of N photons from the field and N_0 is the minimum (or threshold) photon number, which has to be absorbed for ionization. The dominant part of a strong-field photoelectron spectrum (without plateau) extends up to about $2U_p$ before it falls off exponentially. Therefore, the sum over N in equation (1) has to be performed well beyond $N = 2U_p/\omega + N_0$ in order to achieve convergence of the results. In practice, in the actual calculations up to 35 photon orders are taken into account.

We note that the leading-order *S*-matrix approximation has been found earlier to account well for the experimental signals from the diatomic molecules N_2 and O_2 [20], as well as for the hydrocarbons C_2H_2 , C_2H_4 and C_6H_6 [22], but not for the highly electronegative molecules like F_2 [25]. For the present purpose we have therefore restricted our analysis below to linear molecules of C, N and O atoms.

The angular distribution of photoelectron yields is obtained by combining the fundamental rates, equation (1), with the rate equations for the differential yields:

$$\frac{dP_0(\mathbf{r}; t)}{dt} = -W(I(\mathbf{r}; t), \beta)P_0(\mathbf{r}; t) \quad (2)$$

$$\frac{dP_\Omega(\mathbf{r}; t)}{dt} = \frac{dW(I(\mathbf{r}; t), \beta)}{d\Omega}P_0(\mathbf{r}; t) \quad \text{for all } \Omega \quad (3)$$

where P_0 is the probability of finding the target molecule in the initial state, $W(I, \beta) = \int d\Omega dW(I, \beta)/d\Omega$, and P_Ω is the probability of finding the ejected electron in the element of solid angle $d\Omega$. $I(\mathbf{r}, t)$ is the space–time profile of the laser beam. The equations are solved under the constraint $P_0(t) + \int d\Omega P_\Omega(t) = 1$ with $P_0(t = -\infty) = 1$ and the contributions from all points in the laser focus are summed up. For actual computations we have used a Gaussian pulse profile with a peak intensity I_0 and centred around $t = 0$ with a pulse width τ (FWHM) and a TEM₀₀-mode Gaussian beam. We restricted the spatial variation to the axis perpendicular to the propagation direction. The latter corresponds to experimental situations in which the Rayleigh length of the laser beam is significantly larger than the dimensions of the time-of-flight spectrometer.

We consider the angular distributions of photoelectrons emitted from an ensemble having a given minimum cone angle of alignment, β , measured with respect to the polarization direction. This scenario is related, for example, to a two-pulse experiment in which the first pulse is used to align the molecules (to a minimum cone angle β) and a second (ultrashort) pulse is used to ionize it. Assuming that such an ultrashort pulse does not contribute to the alignment of the molecule in a Ti:sapphire laser, we have calculated the angular distributions of the photoelectrons in a short laser pulse ($\tau = 10$ fs (FWHM), $\lambda = 800$ nm) for di- and polyatomic molecules.

In figure 1 we present the results of calculations for N₂ (panel (a)) and O₂ (panel (b)) for a laser peak intensity $I_0 = 10^{14}$ W cm⁻², NO (panel (c)) and C₇ (panel (d)) for $I_0 = 2 \times 10^{13}$ W cm⁻². The fundamental rates, which are used in the rate equations for the yields, are averaged over all possible orientations within the cone angle (cf equation (1)). This angle β provides a quantitative measure of the degree of (adiabatic) alignment, e.g. $\beta = 0^\circ$ corresponds to complete alignment while $\beta = 180^\circ$ corresponds to completely random orientations. In the figures, polar angles are measured from the laser polarization direction $\hat{\mathbf{e}}$ (linearly polarized) in the laboratory frame. The angular distributions of the O₂, NO and C₇ (π -symmetry), on the one hand, and N₂ (σ -symmetry) molecules, on the other, show a characteristic difference. In the case of N₂ molecules the distributions remain unchanged for any degree of alignment. In contrast, O₂, NO and C₇ distributions show the appearance of a node along the polarization axis as the alignment angle is decreased from the random orientations, $\beta = 180^\circ$, toward complete alignment, $\beta = 0^\circ$.

This behaviour can be understood qualitatively as follows. As pointed out at the outset molecules with active orbitals of π -symmetry, like O₂, NO and C₇, possess a nodal plane through the (body-fixed) molecular axis, which leads to a vanishing photoelectron angular distribution along this axis. In a fully randomly oriented ensemble of such linear molecules the minimum along the space-fixed axis due to the molecules that are aligned is washed out by the addition of contributions from the overwhelmingly larger number of molecules that are not oriented along the space-fixed axis. But, for an aligned ensemble of linear molecules the body-fixed axis coincides with the space-fixed axis (alignment axis) and hence the node can show up along the common axis. It might be expected that the influence of the nodal plane would begin to be felt already below a certain cone angle, even when the alignment is not exact. In fact, in the present case the minimum begins to appear for $\beta \approx 30^\circ$ (O₂, NO) and $\beta \approx 15^\circ$ (C₇) and the height of the minimum as a function of β is seen to act as a relative

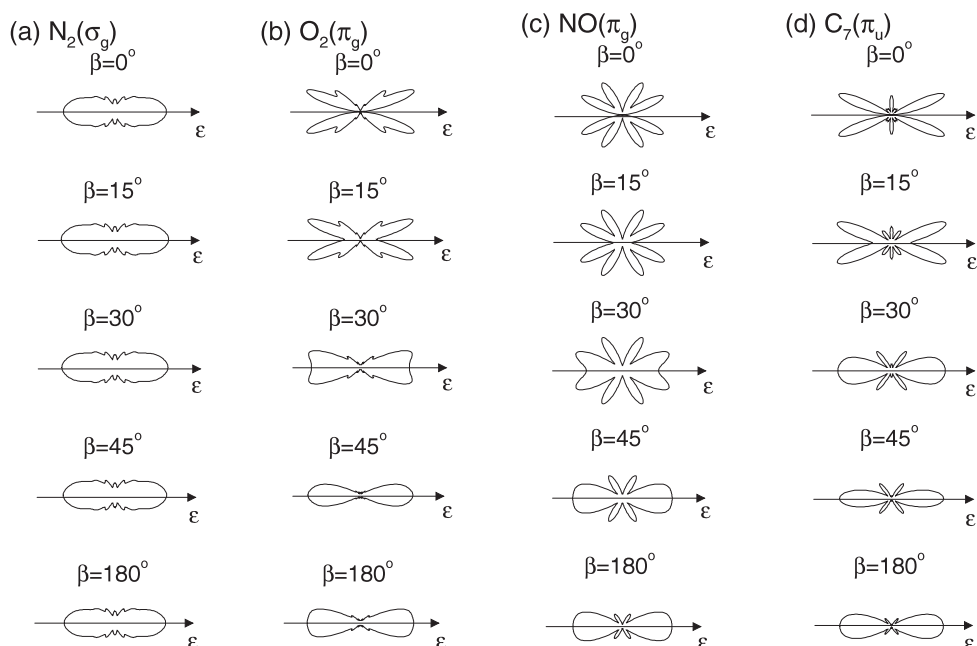


Figure 1. Comparison of angular distributions of electrons from the homonuclear diatomics N_2 and O_2 , the heteronuclear diatomic NO ^{Note 4} and the polyatomic C_7 . Results are obtained for ensembles of molecules at different fixed cone angles of alignment. Laser parameters were $\lambda = 800$ nm, $\tau = 10$ fs and $I_0 = 10^{14}$ W cm^{-2} for panels (a) and (b) and $I_0 = 2 \times 10^{13}$ W cm^{-2} for panels (c) and (d).

measure of the degree of alignment of the ensemble. The above interpretation applies to the whole class of linear molecules having active π electrons, as exemplified in figure 1 for the classes of homo- and heteronuclear diatomics as well as polyatomics.

Since intense-field ionization is a highly nonlinear process, ionization in the parameter domain of interest (e.g. of a typical Ti:sapphire laser system) essentially occurs at the peak of the laser pulse, at different positions in the laser focus. The angular distributions are therefore expected to be dominated by that occurring at the peak intensity of the pulse. It is nevertheless interesting to investigate, if the signature of the nodal minimum is affected, if the alignment angle is made to vary from point to point in the laser focus due to the adiabatic variation of the local intensity. To simulate, only qualitatively, the intensity dependence of the alignment angle $\beta(I(r, t))$ we adopt a slowly varying heuristic model⁵:

$$\beta(I(r, t)) = 180^\circ - (180^\circ - \beta) \cos^2\left(\frac{I_0 - I(r; t) \pi}{I_0} \frac{\pi}{2}\right). \quad (4)$$

Notice that, when the initial intensity is zero, the alignment angle is 180° , corresponding to a completely random distribution of molecular orientations and that for the peak intensity it corresponds to the minimum cone angle β . The angular distribution of the photoelectron yields must now be calculated from equations (1) to (4), taken simultaneously together.

In figure 2 we present the results for $\lambda = 800$ nm and a pulse duration $\tau = 100$ fs for (a) O_2 , $I_0 = 5 \times 10^{13}$ W cm^{-2} , (b) NO , $I_0 = 10^{13}$ W cm^{-2} and (c) C_7 , $I_0 = 10^{13}$ W cm^{-2} . It is

⁴ For the heteronuclear molecule NO the yields for the two distinct positions of the nuclei with respect to the centre of the molecular axis are averaged for each orientation.

⁵ For more elaborate dynamical models see, for example, [26, 27, 13].

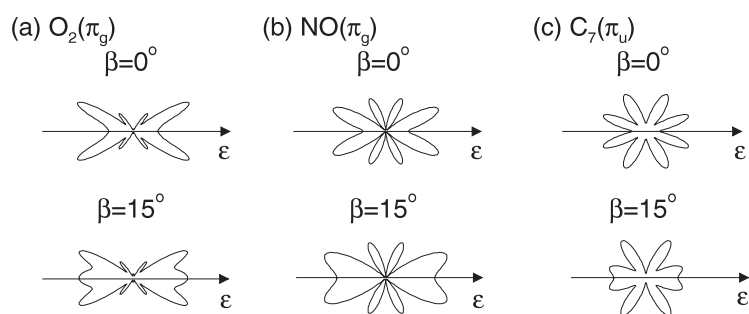


Figure 2. Comparison of photoelectron angular distributions for (a) O_2 , $I_0 = 5 \times 10^{13} \text{ W cm}^{-2}$, (b) NO , $I_0 = 10^{13} \text{ W cm}^{-2}$ and (c) C_7 , $I_0 = 10^{13} \text{ W cm}^{-2}$ calculated assuming an adiabatic intensity-dependent cone angle, equation (4), minimum cone angle β , $\lambda = 800 \text{ nm}$ and $\tau = 100 \text{ fs}$.

seen that the characteristic minimum along the polarization axis is reached for full alignment ($\beta = 0^\circ$) for all molecules investigated. This behaviour is fully consistent with the results shown in the previous figures obtained from the simplified fixed cone-angle calculations and shows that the basic signature of the nodal minimum along the polarization direction for an aligned ensemble is not washed out by averaging over the adiabatic variation of the local intensity in the laser focus. The height of the minimum increases with the decrease in the alignment and, for example, for O_2 the minimum turns into a maximum already at $\beta = 15^\circ$.

In summary, we have shown by an intense-field S -matrix analysis that the photoelectron angular distributions depend strongly on the degree of alignment of the molecular ensemble when a linear molecule having an active orbital of π -symmetry is exposed to an intense laser pulse. The appearance of a nodal minimum along the polarization axis characterizes the variation from random orientation towards complete alignment. This could be observed either in a pump–probe experiment, in which the pump pulse aligns the molecules and the (very short) probe pulse ionizes them, or in a single-pulse ionization experiment with an intense slowly varying laser pulse.

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References

- [1] Bandrauk A D 1994 *Molecules in Laser Fields* (New York: Dekker)
- [2] Posthumus J 2001 *Molecules and Cluster in Intense Laser Fields* (Cambridge: Cambridge University Press)
- [3] Litvinyuk I V *et al* 2003 *Phys. Rev. Lett.* **90** 233003
- [4] Talebpour A *et al* 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L49
- [5] DeWitt M J *et al* 2000 *J. Chem. Phys.* **113** 1553
- [6] Apalategui A and Saenz A 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 1909
- [7] Tong X M *et al* 2002 *Phys. Rev. A* **66** 033402
- [8] Zhao Z X *et al* 2003 *Phys. Rev. A* **67** 043404
- [9] Velotta R *et al* 2001 *Phys. Rev. Lett.* **87** 183901
- [10] Lein M *et al* 2002 *Phys. Rev. Lett.* **88** 183903
- [11] Posthumus J H *et al* 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L553
- [12] Ellert Ch and Corkum P B 1999 *Phys. Rev. A* **59** R3170
- [13] Banerjee S *et al* 2001 *Phys. Rev. A* **63** 045401
- [14] Larsen J J *et al* 1999 *J. Chem. Phys.* **111** 7774
- [15] Seideman T 2002 *Annu. Rev. Phys. Chem.* **53** 41

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- [16] Reid K L 2003 *Annu. Rev. Phys. Chem.* **54** 397
 - [17] Keldysh L V 1964 *Zh. Eksp. Teor. Fiz.* **47** 1945
Keldysh L V 1965 *Sov. Phys.—JETP* **20** 1307 (Engl. Transl.)
 - [18] Faisal F H M 1973 *J. Phys. B: At. Mol. Phys.* **6** L89
 - [19] Reiss H R 1980 *Phys. Rev. A* **22** 1786
 - [20] Muth-Böhm J *et al* 2000 *Phys. Rev. Lett.* **85** 2280
 - [21] Grasbon F *et al* 2001 *Phys. Rev. A* **63** 041402(R)
 - [22] Muth-Böhm J *et al* 2001 *Chem. Phys. Lett.* **337** 313
 - [23] Faisal F H M 1987 *Theory of Multiphoton Processes* (New York: Plenum)
 - [24] Schmidt M W *et al* 1993 *J. Comput. Chem.* **14** 1347
 - [25] DeWitt M J *et al* 2001 *Phys. Rev. Lett.* **87** 153001
 - [26] Friedrich B and Herschbach D 1995 *Phys. Rev. Lett.* **74** 4623
 - [27] Dion D M *et al* 1999 *Phys. Rev. A* **59** 1382