Laser-induced orbital projection and diffraction of O₂ with velocity map imaging

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In a velocity map imaging spectrometer, we measured the electron momentum distributions from the ionization of O₂ molecules with 800 nm wavelength, 40 fs laser pulses at a peak intensity of 2.5×10^{14} W cm⁻². The molecules were aligned at 0°, 45° and 90° relative to the laser polarization prior to ionization. We show that for all alignments the low momentum region – populated by direct electrons which do not recollide with the parent ion – is consistent with the ionized orbital being filtered and projected onto the continuum electron wave packet. In the high momentum region – populated by rescattered electrons – we observe that the pattern created by diffraction of the recolliding wave packet by the ion core disappears as the alignment gets closer to the laser field axis. We find that a two-slit diffraction model agrees well with the results for molecules aligned at 90°, but only partially predicts the decrease in the diffraction signature for smaller alignment angles.

Keywords: velocity map imaging; laser induced electron diffraction; orbital imaging

1. Introduction

The past decade has witnessed great advances in the application of ultrashort, intense laser pulses to molecular imaging. Often these imaging concepts build upon the recollision mechanism: the tunnel-ionized electron wave packet is driven away and back to the parent ion by the oscillating laser field, whereupon it scatters with it [1,2]. While recollision results in elastic as well as inelastic scattering, mainly inelastic scattering as exploited for molecular imaging. In an inelastic collision the parent molecule can be excited into a dissociative state of the singly charged molecular ion [3,4] or even be multiply ionized [5–9] leading to fragmentation of the molecule. This provides a fingerprint of the state of the molecule at the moment of recollision through the kinetic energy of the fragments, much like in Coulomb explosion imaging [10–18]. Likewise, inelastic collision is at the heart of high harmonic emission [1,19]. The observation of high harmonic radiation has been proven to be a very promising approach to molecular imaging [20–25].

The elastically rescattered electron wavepacket, on the other hand, has also been ascribed great potential for molecular imaging [26]. For atoms, it was shown that the structure of the high energy portion of the electron momentum distribution is directly related to the differential elastic scat-

tering cross-section of free electrons with the target [27–29]. In the case of molecules, it was predicted by different authors in the last few years that the rescattered electron could undergo slit-like diffraction via its elastic collision with the different nuclei of the parent ion, which would result in an additional modulation of the final momentum distribution [30–34]. This phenomenon, called laser-induced electron diffraction (LIED) [26], was demonstrated in an experiment by Meckel et al. [35] for aligned N₂ and O₂ molecules and later in other molecules [36–38]. In the Meckel et al. experiment it was discovered that the momentum distribution of electrons that do not (or only weakly) interact with the parent ion reflect the structure of the molecular orbital they originate from.

In this paper we extend the work of Meckel et al. to different alignment angles, i.e. we study O₂ molecules aligned at 0°, 45° and 90° relative to the ionizing laser field. In particular, we find that the modulation in the diffraction structure of O₂ is gradually attenuated as the molecule is rotated into alignment with the ionizing laser field. Using a simple model we interpret this loss of diffraction as a consequence of the asymmetric coulomb field experienced by the recolliding electron wavepacket in an head-on-collision.

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We also show that the low energy part of the electron momentum distribution changes as a function of the alignment in agreement with the tunnelling picture of Meckel et al. [35], i.e. with the rotation of the projected highest occupied molecular orbital (HOMO). Hence, we confirm the potential of the tunnel-ionized electron wave packet's lateral momentum as a probe of molecular orbital geometry.

By employing electron velocity map imaging (VMI) [39] in our experiment we demonstrate that measurements similar to those achieved by Meckel et al. [35] can also be obtained without selecting the ionization channel by detecting the molecular ion in coincidence. At the same time, VMI provides two-dimensional images of the electron momentum distribution with comparatively little data processing. Finally, VMI also permits the detection of many (> 10) electrons per laser shot and MHz laser repetition rates and therefore provides a route to fast LIED imaging

The paper is organized as follows. The experimental setup and methods are described in Section 2. In Section 3.1, we present results for the same molecular alignment geometry as in the experiment of Meckel et al. (molecules aligned 90° relative to the ionizing field versus anti-aligned molecules) and show that we get equivalent results. Results for the two new molecular alignment angles are shown in Section 3.2. We give a detailed explanation of the models that we use to simulate orbital projection and LIED in Sections 4.1 and 4.2, respectively, along with the analysis of the experimental results according to those models.

2. Experimental setup and procedure

The present work was performed at the Advanced Laser Light Source, in Varennes, Québec, using a dual electron-ion momentum spectrometer. The experimental vacuum chamber is made of three differentially-pumped sub-chambers. A continuous gas jet is produced in the first chamber by expanding O_2 through a $50\ \mu\text{m}$ diameter pinhole with ≈ 100 torr of backing pressure. The jet enters the second and third chambers, passing each time through a 1 mm-diameter skimmer. It then goes through the center of the spectrometer assembly (see Figure 1) in the third chamber, where the pressure is maintained around 10^{-9} torr.

The spectrometer assembly is a combination of VMI and ion recoil momentum spectrometer. The upper part of the assembly is the VMI electron spectrometer. It consists of three electrodes 15 mm apart (the repeller, the extractor and the drift tube plate) followed by a 200 mm long drift tube. A 20 mm-diameter hole is drilled in the center of the extractor and the drift tube plate. The gas jet travels halfway between the repeller and the extractor. The laser beam enters the chamber perpendicularly to the gas jet and the spectrometer axis. It is focused in the gas jet with an on-axis $f = 100$ mm spherical mirror. Negative voltages are applied to the repeller and the extractor, whereas the drift tube and its plate are kept grounded. The maximum voltage

Figure 1. Sketch of the dual electron-ion momentum spectrometer used for the experiment. The upper part (1) is a velocity map imaging spectrometer providing a two-dimensional image of the momentum distribution of electrons produced at the laser focus. The lower part (2) is a constant field time-of-flight spectrometer with position-sensitive detector allowing measurement of the three components of the momentum vector of each ion produced at the laser focus. The electron and ion spectrometers are not designed to be operated simultaneously.

that can be applied on the repeller is 15 kV. In VMI a ratio of the voltages at extractor and repeller plate of 0.72 has been found to yield the optimal focusing geometry. Hence, an image of the two-dimensional velocity distribution at the laser focus can be obtained, independent of spatial extent of the focus. The electrons hit a detector made of 80 mm diameter microchannel plates and a phosphor screen (Burle electro optics). The image on the screen is recorded with a 14 bit CCD camera located outside the chamber.

The lower part of the assembly is the ion recoil momentum spectrometer. A hole with a diameter of 6 mm is drilled in the center of the repeller. Below it, a set of evenly 1 cm spaced 20 rings forms the ion flight region, completed at the end by a 90 mm-diameter time-and-position-sensitive detector [40] (Roentdek), made of microchannel plates and delay-line anodes. When the ion spectrometer is used – which can not be used simultaneously with the electron spectrometer – a nearly-uniform electric field (up to $20\ \text{kV m}^{-1}$) is created from the drift tube plate down to the detector. From its time-of-flight and its impact position on the detector, the three components of each ion's momentum vector following laser ionization can be determined.

The measurements were done with a Ti:Sapphire laser system (Thales) providing 30 fs pulses at a wavelength of

Figure 2. (a) Molecular alignment parameter $\langle \cos^2 \theta \rangle$ around the 1/4-revival measured for O_2 as a function of pump-and-probe delay. (b) Distribution of molecular orientations relative to the aligning field polarization axis for delays corresponding to alignment (3.0 ps) and anti-alignment (2.6 ps) of O_2 . (The color version of this figure is included in the online version of the journal.)

785 nm with a repetition rate of 100 Hz. The pulses were divided into two parts with a beamsplitter and recombined before entering the chamber collinearly. While separated, one beam was reflected on mirrors placed on a translation stage, thus enabling control of the timing between each pulse. The polarization state of each beam is controlled by waveplates before they are recombined on a near-zero degree of incidence beamsplitter. They are then steered to the target chamber by two mirrors with small angles of incidence ($<10^\circ$), which allows for good preservation of each beam's polarization state.

In the preparation of the experiment, the right conditions for alignment of the O_2 molecules were determined with the ion momentum spectrometer. The first (pump) laser pulse was stretched to 200 fs by a 13 mm thick SF6 block and focused into the gas jet to a peak intensity of $4 \times 10^{13} \text{ W cm}^{-2}$. Such a pulse does not significantly ionize O_2 , but induces a rotational wave packet in the gas. This leads to transient molecular alignment along the polarization axis shortly after it has passed, followed by alignment revivals occurring at regular time intervals [10]. The degree of molecular alignment was monitored by Coulomb exploding the molecules with a second, circularly polarized (probe) pulse at an intensity of $5 \times 10^{14} \text{ W cm}^{-2}$ and 40 fs duration. Measurement of the momentum vector of the O_2^+ fragments allowed the determination of the distribution of molecular orientations within the polarization plane as a function of pump-probe delay. We concentrated on the first recurrence of molecular alignment (1/4-revival) occurring 3.0 ps after the pump pulse. Figure 2(a) shows the evolution of $\langle \cos^2 \theta \rangle$ between 2.3 ps and 3.5 ps, where θ is the angle between the projection of the molecular axis in the probe pulse's polarization plane and the aligning pulse's polarization axis. In this time window, $\langle \cos^2 \theta \rangle$ is initially around 0.5, meaning that the distribution of molecular orientation is nearly isotropic. The parameter then drops to 0.41 near 2.6 ps and

peaks at 3.0 ps with a value of 0.74. The distribution of molecular orientations within the probe laser polarization plane is shown for those two points in Figure 2(b). The highest $\langle \cos^2 \theta \rangle$ value corresponds to molecular alignment, for which most molecules are oriented along the aligning laser field's axis. The opposite case is anti-alignment, for which molecules lie mostly in the plane perpendicular to the aligning field's axis.

For the main experiment, the aligning pulse was kept with the same conditions whereas the probe was changed to linear polarization with an intensity of $2.5 \times 10^{14} \text{ W cm}^{-2}$ in order to single ionize O_2 . The method consists of recording the electron momentum distribution with the VMI spectrometer for a case of molecular alignment and comparing it to a reference momentum distribution recorded for the case of anti-alignment. For the first set of measurements, the molecules were aligned perpendicular to the ionizing laser field, while the anti-aligned molecules were lying in the plane perpendicular to the alignment axis, as was done by Meckel et al. [35]. In the other set of measurements, the distributions were recorded for molecules aligned at 45° and 0° with respect to the probe laser field, while the reference was unchanged.

3. Results

3.1. Alignment perpendicular to ionizing field

We begin by presenting the experimental results obtained with orthogonal polarizations of pump and probe beams. This configuration is identical to [35] and in the following we will refer to it as 90° -alignment. To describe the experimental geometry, we use a coordinate system that is defined by the ionizing, i.e. the probe laser pulse. The polarization of the probe pulse determines the Z-axis whereas the direction of beam propagation defines the X-axis. Figure 3(a) and (d) sketch the molecular orientation distributions with

Figure 3. Sketches of the molecular alignment geometries used in the experiment. The green and red arrows point in the direction of the aligning and ionizing laser polarizations, respectively. Molecules aligned at (a) 90°, (b) 45° and (c) 0° relative to the ionizing field. (d) Molecules anti-aligned in the plane perpendicular to alignment axis at 90° relative to the ionizing field. (The color version of this figure is included in the online version of the journal.)

respect to the pump and probe fields for 90°-alignment and the corresponding anti-alignment, respectively: at 90°-alignment the molecules are oriented mostly perpendicular to the ionizing laser field (around the Y -axis), whereas for anti-alignment the molecules lie predominantly in the XZ -plane. Figure 3(b) and (d) illustrate the other two alignment geometries investigated in this work.

In VMI only two-dimensional distributions are recorded while the third dimension is integrated. To access the third dimension the laser polarizations of both pump and probe beams need to be rotated. Note, that VMI typically does not provide access to the ZY -plane which is normal to the beam propagation axis.

For the 90°-alignment geometry we recorded the two projections in the XY and ZX plane as shown in Figure 4(a) and (b), respectively. For each projection we recorded the electron momentum distribution for both alignment (at a pump–probe delay of 3.0 ps) and anti-alignment (at a delay of 2.6 ps). The two pump–probe delays were switched every five minutes, in order to average over slow fluctuations of the laser conditions. Each projection of the momentum distribution was recorded during about 15 h corresponding to approx. 3×10^6 laser shots per alignment.

Figure 4(a) and (b) exhibit a drop of five orders of magnitude in the electron yield from the peak at zero momentum to the edges of the distribution. The distributions obtained for anti-aligned molecules are not shown, since they are indistinguishable from the aligned case.

The measurement with the ionizing field parallel to the detector (Figure 4(b)) has been integrated along each axis to give one-dimensional distributions. The momentum distribution along the ionizing field axis (p_z), shown in Figure 4(d), exhibits two distinct regions. Up to about 2.0 au (atomic units), the distribution is dominated by the direct electrons, i.e. the part of the electron wave packet that does not reencounter the parent ion after ionization or is deflected only under small scattering angles. This distribution corresponds to the mapping of the dependence of the ionization rate on the electron phase of birth in the oscillating laser field into the electron's final longitudinal momentum. Beyond a momentum of 2.0 au the distribution is dominated by that

part of the wave packet that rescatters off the parent ion and thereby picks up extra momentum. This region corresponds to the plateau in above-threshold-ionization spectra [41]. In the momentum component perpendicular to the ionizing field (p_x), shown in Figure 4(c), the transition between those two different regimes is also visible at around 0.5 au.

Modulations of the electron momentum distribution due to the molecular orientation relative to the ionizing laser field can hardly be distinguished in individual measurements. Only direct comparison of the distributions for different molecular orientations reveals structure. We compute the normalized difference in the doubly differential electron yield $\partial^2 N \equiv \partial^2 N / (\partial p_x \partial p_y)$ between the 2-d distributions obtained for alignment ($\partial^2 N_{AL}$) and anti-alignment ($\partial^2 N_{AA}$), expressed as

$$\partial^2 N_{ND} = \frac{\partial^2 N_{AL} - \partial^2 N_{AA}}{\partial^2 N_{AL} + \partial^2 N_{AA}}. \quad (1)$$

In Figure 5(a) and (b) the normalized differences of the XY and ZX projections are shown, respectively. In both projections, the areas corresponding to the direct and rescattered electrons are noticeably different. In the XY projection, shown in Figure 5(a), the pattern created by the direct electrons ($(p_x^2 + p_y^2)^{1/2} < 0.5$ au) reveals a clover leaf-like structure with maxima along p_y (axis of the aligned molecules) and minima along p_x (axis along which the anti-aligned distribution is projected). In the plane parallel to the ionizing field (Figure 5(b)), this pattern is projected along p_x . Within -1.5 au $< p_z < 1.5$ au it is nearly constant, indicating that it is independent of the electron phase of birth.

In the same projection, the area of high momentum dominated by the rescattered electrons has maxima centered at $p_z = 0$ au and $p_x = \pm 1.0$ au, as well as at $p_x = 0$ au and $|p_z| > 2.0$ au. It also has minima at $p_x = \pm 1.2$ au and $p_z = \pm 1.6$ au. In the XY projection (Figure 5(a)), the pattern has maxima at $p_x = \pm 1.0$ au and $p_y = 0$ au, corresponding to the maxima at $p_z = 0$ au and $p_x = \pm 1.0$ au in Figure 5(b). It has been seen in the measurements done by Meckel et al. [35] that the pattern in the p_y – p_z plane (which cannot be observed with the VMI apparatus) is reversed with respect to what is seen in the p_x – p_z plane, because of the symmetry between the 90°-alignment and anti-alignment distributions. Hence, we know that the minima at $p_x = 0$ au and $p_y = \pm 1.0$ au correspond to minima at $p_z = 0$ au and $p_y = \pm 1.0$ au.

3.2. Other molecular alignments

In this section, we present measurements for which the molecules were aligned at 45° and at 0° with respect to the laser field, as sketched in Figure 3(b) and (c), respectively. Those measurements have only been performed in the ZX projection. Each alignment distribution contains approx. 2×10^6 laser shots. For the further analysis of the data we

Figure 4. Electron momentum distribution for molecules aligned perpendicular to the ionizing field, with this field being (a) parallel and (b) perpendicular to the detector plane. (c) One-dimensional distribution parallel to the ionizing field obtained from integration of the distribution shown in (a). (d) One-dimensional distribution perpendicular to the ionizing field, based on (b). Results for other molecular alignments (not shown) appear almost identical on these types of plot. (The color version of this figure is included in the online version of the journal.)

Figure 5. Normalized difference between measurements 90°-aligned and anti-aligned molecules. The ionizing laser field is (a) perpendicular and (b) parallel to the detector plane. (The color version of this figure is included in the online version of the journal.)

normalized the 0°-alignment and 45°-alignment distributions with the anti-alignment distribution (see Figure 3(d)).

The normalized difference graphs for both alignments are presented in Figure 6. The contrast in both measurements

Figure 6. (a) Normalized difference ∂_{ND} between measurements for molecules aligned at 45° and anti-aligned. (b) Same for molecules aligned at 0° and anti-aligned. The ionizing laser field is parallel to the detector plane. (The color version of this figure is included in the online version of the journal.)

is lower than for the 90°-alignment. However, in the area covered by the direct electrons, the pattern is qualitatively different. For molecules aligned parallel to the ionizing field (Figure 6(b)), the pattern appears reversed: at $p_x = 0$ au the relative electron yield shows a minimum for all p_z . On the other hand, in the 45°-alignment (Figure 6(a)) the distribution at $p_x = 0$ au still retains the character of a maximum from the 90°-alignment.

In the area of rescattered electrons, the general pattern does not change when the angle of molecular alignment is rotated. Instead, it seems that the contrast is gradually diminished. Hence, while at 45°-alignment, the pattern, although barely discernible, is similar to the 90°-alignment, it is not detectable when the molecules are aligned parallel to the ionizing laser field.

The reasons for the changes in the direct and rescattered electron areas of the normalized difference plots with molecular alignment will be discussed in the following section.

4. Analysis

4.1. Direct electrons

According to tunnelling theory [42–44], when a molecule is ionized in a strong laser field, the orbital from which the electron is removed – generally this is the HOMO – is filtered and mapped onto the lateral momentum of the liberated electron wave packet. The lateral component of the continuum state momentum wave function is given (in atomic units) by [31]:

$$\Psi_f(p_\perp) \propto \Psi_i(p_\perp) \exp\left(-\frac{I_p^{1/2}}{2^{1/2}E} p_\perp^2\right) \quad (2)$$

where Ψ_i is the momentum space representation of the ionizing orbital and the exponential factor is the filter function of the tunnel, with I_p being the molecular ionization potential and E the laser field at the time of tunnelling.

Since the laser field only acts upon the electron along the polarization direction, the lateral structure of electron

wave packet largely survives its subsequent propagation in the laser field, giving rise to the observed modulation in the direct electron's lateral momentum distribution. We now confirm this idea through a numerical simulation.

The first step of the modelling is to compute the tunnel-filtered projection of the HOMO of O_2 for many different angles between the molecular axis and the ionizing field. This was achieved by calculating the configuration-space wave function of the HOMO of groundstate O_2 using GAMESS [45] and computing Equation (2) from its Fourier transform. The HOMO of O_2 has π_g symmetry and is hence composed of two degenerate sets of lobes lying in orthogonal planes through the molecular axis as illustrated in Figure 7(a). However, the laser field can not only lift the degeneracy between the two orbitals but even mix them. Hence, the electron will be ionized preferentially from that part of the field free orbital that is closest to the suppressed barrier. By applying Equation (2) to arbitrarily oriented molecules we calculate the lateral distribution of the tunnelled electron wave packet at the moment of ionization. In Figure 7 we show these tunnelled wave packets in momentum space for three alignment angles. When the molecule is perpendicular to the ionizing field (Figure 7(a)), the electron wave packet has two peaks at a lateral momentum of $p_\perp = 0.35$ au in the direction of the molecular axis; the ionization rate for $p_\perp = 0$ au is zero. As the molecule is rotated towards alignment with the ionizing field, one of the peaks increases in amplitude (the one corresponding to the lobe closer to the tunnel's exit) and moves closer to $p_\perp = 0$ au, while the other one vanishes. For an angle of 55° (Figure 7(b)), one lobe of the orbital is directly in line with the tunnel. Only one peak is visible at $p_\perp = 0$ au. If the direction of the ionizing field coincides with the molecular axis (Figure 7(c)), both p-orbitals become degenerate again, and hence a rotationally symmetric wave packet appears from the tunnel, with a node at the origin.

A more quantitative understanding of the experimental data can be obtained when accounting for the fact that each alignment consists of a distribution of molecular

Figure 7. Lateral momentum distribution of the electron wave packet after tunnelling ionization from an O_2 molecule, calculated for different angles between the laser field and the molecular axis. The sketch in the upper left corner depicts the coordinate system used in the plots. (The color version of this figure is included in the online version of the journal.)

orientations. For this purpose we extended a previously published semi-classical model [46] to include the full alignment distribution as measured by the experiment. The model simulates the ionized electron classically in the combined laser field and the parent ion's potential using a velocity-Verlet algorithm. For every molecular orientation within an alignment distribution the initial conditions for each electron are determined through the instantaneous molecular tunnel ionization rate [47] and the lateral momentum distribution according to Equation (2). The initial longitudinal momentum is assumed to be zero.

The dependence of the ionization rate on the molecular orientation relative to the laser field was estimated using the molecular ADK theory [47], which is known to give results close to experimental observations for O_2 [48]. The tunnel ionization rate of O_2 is strongly peaked around 45° relative to the molecular axis, with minima at 0° and 90° [8,49–52]. This is a direct consequence of the orbital filtering in the tunnelling process. When the molecule is oriented at about 45° , the tunnel is in front of an orbital wave function region of high density, allowing for a larger fraction of it to be ionized compared to when the molecule is oriented parallel or perpendicular to the laser field.

For a better insight of the effect of averaging over a distribution of molecular orientations, we first discuss the averaged wave packet lateral momentum distributions immediately at the exit of the tunnel. We show in Figure 8(a) and (b) these distributions for 90° -alignment and anti-alignment, computed along p_x and p_y , respectively. An obvious feature is the fact that the orientation-averaged curves look perfectly Gaussian; i.e. the nodal structure of the orbital has been wiped out by the averaging. However, the distribution widths are different: the distribution from

the anti-aligned molecules is wider than the one from the aligned molecules along p_x , whereas the reverse is true along p_y . This is in agreement with the experimental results shown in Figure 5(b).

Figure 8 also shows the influence of propagation on the observable momentum distribution. The computed distributions become very narrow and have a cusp-like shape, as a consequence of Coulomb focusing [46]; when the electron wave packet revisits the parent ion. Due to the lateral spread the largest parts of the electron wave packet are scattered at small angles, and are actually pulled inward laterally by Coulomb attraction. This leads to an increase of the wave packet density near zero lateral momentum and thus to the observed cusp. However, the calculations seem to overestimate the strength of Coulomb focusing, since the measured distributions are not as narrow. The calculations nonetheless show that the difference in width between the distributions from aligned and anti-aligned molecules, along both lateral axes, survives wave packet propagation, in accordance with experiment.

In Figure 9 we analyse the momentum component p_x for the three alignment geometries of the experiment. The simulations are shown along with corresponding projections of the experimental results. For the simulated as well as for the experimental results, the normalized difference was computed after integrating along p_z . In the low momentum region, $p_x < 0.3$ au the simulation agrees very well with the experiment. However, for p_x greater than about 0.3 au, the experimental curves depart from the calculated ones. This could be because at this point the distribution already starts to be partly populated by rescattered electrons, which are deflected with a relatively large angle by the ion core and are not accurately treated in the model.

Figure 8. Comparison of photoelectron momentum distribution in the two directions perpendicular to the ionizing field for 90° alignment and anti-alignment. (a) p_x , (b) p_y . Compared are the simulated distributions after tunneling, and after propagation, as well as the experimentally obtained distributions. (The color version of this figure is included in the online version of the journal.)

Figure 9. Comparison of experimental and simulated photoelectron momentum distributions perpendicular to the ionizing field. (The color version of this figure is included in the online version of the journal.)

4.2. Rescattered electrons

The electrons that populate the rescattering region of the momentum distributions are those that revisit the parent ion with small impact parameter and strongly interact with it. This part of the wave packet undergoes diffraction through collision with the two-center core. In order to analyze the diffraction patterns observed in our measurements, we consider an electron plane wave of momentum p_i with intensity I_0 being scattered by a rigid molecule with a final momentum p_f . The scattered intensity of the electron wave $I(s)$ is given by the following formula, as a function of the momentum transfer vector $s = p_i - p_f$ [53]:

$$I(s) \propto I_0 \sum_{m=1}^N \sum_{n=1}^N f_m(s) f_n^*(s) \exp(is \cdot r_{mn}). \quad (3)$$

In this expression, N is the number of atoms in the molecule, r_{mn} is the vector linking the m th with the n th atom in the molecule and $f_m(s)$ is the atom's scattering factor. In the case of O_2 , $N = 2$ and there is only one scattering factor involved. The equation can then be written

as follows, d being the vector joining the molecule's nuclei:

$$I(s) \propto I_0 |f(s)|^2 [1 + \cos(s \cdot d)]. \quad (4)$$

We now neglect $f(s)$, since we assume it is constant and it is therefore cancelled in the normalized difference. We consider only electron scattering within the X - Z plane and assume that it dominates our measurements of the p_x - p_z momentum distributions. For an electron incoming with momentum p along the laser field axis (Z) and being scattered at an angle θ_e by a molecule oriented with an angle θ_m relative to the Z -axis and with azimuthal angle φ_m relative to the X -axis, Equation (3) becomes (in atomic units):

$$I \propto I_0 \left[1 + \cos \left(pd(\sin \theta_e \sin \theta_m \cos \varphi_m + (\cos \theta_e - 1) \cos \theta_m) \right) \right]. \quad (5)$$

This equation gives the diffracted intensity versus scattering angle for a given rescattering momentum. We must now connect this to the final momentum space in which measurements were done. Analysing the electron wave packet with classical trajectories [1], the electron rescattering momentum p_{rec} is calculated as a function of the phase of birth in the laser field. The electron scattered at an angle θ_e keeps its momentum immediately after the impact and is thus mapped in momentum space along a circle of radius p_r centred on zero. After hitting the ion, the electron keeps moving in the field and gains extra momentum $p_{\text{streak}} = (E_0/\omega_L) \sin \phi_r$, where E_0 is the laser field's amplitude, ω_L is the laser angular frequency and ϕ_r is the field's phase at the moment of rescattering. The center of the rescattered electron's momentum circle is thus translated by p_{streak} along the field's direction [31]. We analyse LIED along such diffraction circles, illustrated in Figure 10(a), using Equation (4). These circles are those of the long trajectories. They dominate over the short ones because of their higher ionization rate, despite the fact that they spend a longer time

Figure 10. (a) Normalized difference (ND) for 90° alignment. Indicated are regions of constant recollision momentum (for $p_y = 0$): 1 au, 1.2 au and 1.4 au in black, red and blue, respectively. (b)–(d) Angular yield of ND along circular cuts for constant recollision momentum as indicated in (a), measured in the experiment. Parts (e)–(g) are corresponding angular distributions obtained with our simulation. (The color version of this figure is included in the online version of the journal.)

spreading in the field before rescattering. The only other assumption that we make is that the scattering momentum to be used in the diffraction formula corresponds to the kinetic energy of the classical trajectory electron plus the ionization potential of the molecule: $p = [2(p_{\text{rec}}^2/2 + I_p)]^{1/2}$. Numerical calculations [30,32] and experiment [54] have shown that this is the effective kinetic energy with which the rescattering electron wave interacts with the ion core. The diffraction curves calculated along the circles were averaged over the distributions of molecular orientation, taking the recollision rate (giving I_0), into account. The recollision double ionization rate depends on the combined influence of the angle-dependent ionization rate and the electron wave packet lateral momentum distribution, since only the part of the wave packet with close to zero lateral momentum revisits the core. For molecules parallel or perpendicular to the laser field, the wave packet has no density for zero lateral momentum (see Figure 7) and thus the double ionization rate is strongly suppressed [8].

Line outs along the diffraction circles illustrated in Figure 10(a) were extracted from the normalized difference plots in the p_x – p_z plane from the experiments with the three different molecular alignments (Figure 5(a) and Figure 6(a)–(b)). These are shown in Figure 10(b)–(d). The line outs were extracted only for scattering angles $30^\circ < \varphi < 330^\circ$, because the area outside of this range is populated by direct electrons. The corresponding curves calculated with the diffraction model explained above are shown in Figure 10(e)–(g). As was already shown by Meckel et al. [35], our model describes the experimental results quite well in the case where molecules are aligned at 90° relative to the laser field. It correctly predicts the position of the diffraction maxima ($\varphi \approx 60^\circ$ and 300°) and minima ($\varphi \approx 120^\circ$ and 240°), as well as the height of those peaks. Only backscattering ($150^\circ < \varphi < 210^\circ$) is not described properly by the model in this case. However, the agreement between the experiment and the calculation is much poorer in the case of the two other molecular alignments (45° and 0°). The model does predict that the contrast of the diffraction curves should decrease as the angle between the laser field and molecular alignment gets smaller, but not as much as is observed in the experiment.

How can the discrepancies between the model and the experiments be explained? Let us first examine some of the assumptions made in the model. First, the model considers only electron rescattering within the plane of measurement. The results are in fact a projection of all scattering events in three dimensions, but the electron yield drops so rapidly with lateral momentum that it is reasonable to consider that only electrons with small out-of-plane momentum contribute significantly to the observed signal. Furthermore, it seems unlikely that the two-dimensional approximation would produce accurate results in one case (molecules aligned at 90°) and not in the others. Another issue is the angle-dependent recollision probability, which according

to our model very much favours the molecules oriented at an angle around 40° . This selection contributes to making the calculated diffraction curves not changing much with molecular alignment. The model takes into account only the first electron recollision and it is possible that some subsequent recollisions enhance the recollision rate for perpendicular or parallel molecules. The recollision rate could also be different if there is a dependence of the electron scattering cross-section on molecular orientation. However, even if the recollision rate was not angle-dependent, the decrease of contrast predicted by the model for parallel alignment would not match the experimental results. The most severe approximation in our model might be the assumption of a plane wave for the electron before and after the scattering. Such a plane wave approximation is known to become reasonable only for electron energies in the keV regime. Our recollision energies were at most 50 eV. Thus, the qualitative agreement of our data with the model is actually surprising.

We now compare our model with a LIED simulation performed by solving the time-dependent Schrödinger equation (TDSE) in two dimensions (2D) for the ionization of a model O_2 -like H_2^+ molecule. The technical details of the simulation were published for the case of a perpendicular H_2^+ molecule by Spanner et al. [31]. Here, we use a bond length of 2.3 au, intensity of $2.5 \times 10^{14} \text{ W cm}^{-2}$, and the simulation is stopped after the first recollision. To obtain a symmetric momentum space distribution the result is mirrored.

In Figure 11 the electron momentum distribution for different alignments between molecule and ionizing field is shown. While LIED induced minima are clearly visible at 90° alignment there is no distinct modulation to be seen for 60° and 30° . Since the TDSE calculation ignores the experimentally unavoidable intensity averaging and the imperfect alignment distribution, LIED can be observed in the simulation without normalization to the anti-aligned ensemble. As in Figure 10(a) we indicate the diffraction circles of equal recollision momentum $p_r = 1.0, 1.2, 1.4$ au for the long trajectories.

Figure 12(a) shows the ionization yield along the diffraction circles for each recollision momentum p_r in analogy to the experimental data in Figure 10(b)–(d). We analysed the simulation for short trajectories at even higher recollision momentum, in order to identify the influence of either set of trajectories on the experiment. Figure 12(b) shows the short trajectory-analysis for momenta $p_r = 1.5, 1.6, 1.7$ au. (The maximum recollision momentum at $2.5 \times 10^{14} \text{ W cm}^{-2}$ is $p_r = 1.85$ au.) The comparison with experimental data at 90° and 0° reveals a qualitative agreement with the long trajectories, in particular for the lowest recollision momentum.

Also shown in Figure 12 are upward and downward pointing arrows that indicate the position of diffraction minima and maxima, respectively, which were obtained with the model shown in Figure 10(e)–(g). In all cases, the position

Figure 11. Photoelectron momentum distributions obtained by solving the 2D TDSE for a O_2 -like H_2^+ molecule. The bond length is 2.3 au and the intensity $2.5 \times 10^{14} \text{ W cm}^{-2}$. Shown are also the diffraction circles for the long trajectories at $p_r = 1.0$ au (black), $p_r = 1.2$ au (red) and $p_r = 1.4$ au (blue). (The color version of this figure is included in the online version of the journal.)

Figure 12. Calculated angular photoelectron yield along circular cuts as indicated in the 2D molecular-frame photoelectron momentum distribution in Figure 11. (a) Cuts corresponding to long trajectories, as in Figure 10. (b) Cuts corresponding to short trajectories. Upward and downward pointing arrows indicate the position of minima and maxima, respectively, as predicted by our model calculation shown in Figure 10(e)–(g). (The color version of this figure is included in the online version of the journal.)

of the diffraction maxima and minima is in close agreement with that predicted by the model used to analyse our experiment. However, while our model always assumes full contrast between minima and maxima (the intensity of

minima being zero), the contrast in the TDSE simulations varies. It is high for parallel or perpendicular molecules, but much reduced for molecules oriented at 30° relative to the laser field. This shows that even for the simple case

of H_2^+ , LIED can be attenuated depending on molecular orientation. Nothing proves that the variation of diffraction contrast observed in these TDSE simulations would be the same in the case of O_2 , but we note that it would help explain our results, since for alignment at 0° , the average molecular angle in the distribution is close to 30° .

It is difficult to identify one particular cause for the reduction of diffraction contrast in the TDSE calculations. One possible cause is the distortion of the electron wave packet, causing it not to rescatter like a plane wave. Distortion can be due to the orbital wave function being projected onto the wave packet as discussed in this paper. The wave packet can also be distorted as it leaves the ion by the Coulomb potential tail and the bound orbital polarization, which depends on molecular orientation. The diffraction contrast could also be reduced by destructive interference from the short electron trajectories. Comparison of our model with the TDSE simulations have shown that the long trajectories dominate, like we have assumed, but the short ones could still contribute enough to reduce contrast for some molecular orientations.

Another effect that could potentially destroy diffraction is multiple scattering, i.e. electron trajectories being affected by both nuclei in a recollision event. Classically, an electron of momentum p incident on a particle of charge q with impact parameter b is scattered at an angle θ given by $\tan(\theta/2) = b_c/b$. The critical impact parameter $b_c = q/p^2$ corresponds to a scattering angle of 90° . In the TDSE simulations, a typical electron recolliding on a nuclei with a momentum of 2 au has a critical impact parameter of 0.25 au. This is about an order of magnitude smaller than the 4 au bond length of H_2^+ in the simulation, hence the contribution of multiple scattering is likely to be small. However, in the experiments the critical impact parameter of an electron rescattering with momentum p is 0.35 au, which is closer to the O_2 bond length of 1.2 au. Multiple scattering and a shape resonance could thus have a significant impact in this case. Finally, in the case of O_2 , the electrons coming back to the core are scattered by both the nuclei and the electron cloud. Motion of the electron cloud in the laser field could affect the symmetry of electron scattering off the two nuclei and alter the diffraction effect, depending on molecular orientation.

5. Conclusion

Measuring the electron momentum distribution from intense laser ionization of O_2 aligned at 0° , 45° and 90° relative to laser field polarization (and referencing them to measurements obtained from anti-aligned molecules), we have demonstrated that in all cases the lateral momentum of the direct electrons results from the molecule's HOMO being filtered and projected into the electron wave packet

liberated during tunnelling ionization. By taking many such measurements while rotating molecular alignment in small steps, one could then perform tomography of the ionized molecular orbital. The measurements contain all the necessary information about the orbital, with the exception of its phase. In order to complete this task, one would need to develop a reconstruction algorithm that takes into account the molecular alignment distributions and the dependence of the ionization rate on the molecule's orientation (which can be measured simultaneously). To obtain a more faithful reconstruction, it is also desirable to remove the effect of Coulomb focusing on the orbital image imprinted in the electron wave packet. This can be done either by using circularly polarized light to avoid any recollision or by observing the lateral momentum at a high longitudinal momentum, corresponding to electrons that either did not come close to the parent ion or passed by it with high energy, thus reducing Coulomb focusing.

The measurements also allowed observing the change of the diffraction pattern in the momentum space area covered by the rescattered electrons as the angle of molecular alignment was varied. This pattern was seen to disappear as molecular alignment was rotated toward the direction of the ionizing laser field. The plane wave diffraction model that we used to analyse the results correctly predicts the diffraction maxima and minima for perpendicular molecular alignment, but does not satisfactorily explain the disappearance of the diffraction pattern for parallel alignment. Comparison with TDSE calculations for the ionization of H_2^+ have shown that even in this case the diffraction contrast is not as high as predicted by the classical model for some molecular orientations. The reasons for the loss of diffraction contrast are not clear and require further investigation. It would also be interesting to measure the effect of the molecular alignment angle on the diffraction circles pattern in the plane that is not accessible in the VMI machine (p_y – p_z). In that plane, for any molecular alignment other than 0° or 90° , diffraction should lead to patterns that do not have reflection symmetry about the p_z axis, providing another way to test LIED models.

Laser-induced orbital projection and electron diffraction have great potential for studying ultrafast molecular motion, offering the opportunity to observe changes in the shape of the HOMO and nuclear structure simultaneously. It could also prove to have advantages over other strong laser field methods to image larger molecules. Complete imaging of the nuclear structure through Coulomb explosion, either triggered by recollision or not, requires breaking the molecules in a large enough number of pieces, which can be hard to do for complex molecules. By contrast, LIED could give information about the position of many nuclei in a single image.

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