Influence of molecular structure on double ionization of N_2 and O_2 by high intensity ultra–short laser pulses

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Abstract

The electron momentum correlation after non-sequential double ionization of N_2 and O_2 in ultra-short light pulses at light intensities near $1.5\times10^{14}\,\mathrm{W/cm^2}$ has been investigated. The experimental results reveal distinctive differences between the molecular species and between molecules and atoms of similar ionization threshold. We provide evidence that recollision double ionization is the essential mechanism and trace the origin of the differences back to the symmetry of the orbitals occupied by the leuchtelectrons.

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Double ionization of an atom in high intensity ultra-short light pulses proceeds via different pathways: Either, the atom may be ionized step by step via an intermediate singly charged ion. Or it is ionized non-sequentially where the emitted photoelectrons exchange energy before they appear in the continuum simultaneously. The signature of non-sequential double ionization (NSDI) is an unexpected high double ionization probability for moderate light intensities [1]. Detailed investigations have shown that electron impact ionization [2] plays a decisive role [3–7]. Put in simple words, NSDI starts with the release of one electron which is subsequently accelerated by the electric field of the light wave. Under certain conditions, the electron revisits the ion core within the same optical cycle in which it was released. The kinetic energy E_{kin} of the electron upon return can exceed the photon energy by more than an order of magnitude. Depending on E_{kin}, an inelastic collision can either result in instantaneous impact ionization or in electronic excitation of the ion. The excited electron then can easily be removed by the intense light pulse [7].

Similar to atoms simple two-atomic molecules such as N_2 and O_2 also show an excessive double ionization probability indicative of NSDI [8–11]. However, the *total* ion-yield data are not sufficient to identify the mechanism. The presence of revisiting electrons, which are at the basis of atomic NSDI, was recently reported for molecular hydrogen [12, 13]. Thus, one may expect that electron scattering is also the main mechanism for molecular NSDI in general.

In this letter we investigate double ionization of N_2 and O_2 *differentially* in order to identify the non-sequential mechanism and to investigate possible effects of the initial state on the final electron momentum distribution. Single ionization experiments showed that these molecules show a distinctly different behavior. With respect to total ion yield as a function of intensity [9] and electron kinetic energy spectra [14], N_2 behaves like the noble gas atom Ar which has virtually the same ionization potential. On the other hand O_2 and Xe also having similar ionization potentials differ clearly. Ionization of O_2 is suppressed with respect to Xe [9, 15] with the photoelectron spectra showing a diminished electron yield at small and high kinetic energies [14]. These effects have been attributed to the different symmetry of the ground state orbitals occupied by the leuchtelectron [14, 16]. It is of σ_g (bonding) type for N_2 and π_g (antibonding) for O_2. This indeed is able to account for the experimental findings [14, 16]. However, also a charge-screening correction to tunnel ionization was suggested to explain the phenomenon [17]. Recent experimental data even

seem to indicate that neither charge-screening nor initial state orbital symmetry is sufficient to quantitatively predict single ionization of diatomics in general [18].

Here we show that also NSDI depends sensitively on the molecular species. The differential data of O_2 even lack the signatures considered to be characteristic for NSDI. Most surprisingly, however, a simple classical model based on electron recollision double ionization is able to reproduce qualitatively the experimental findings *if* the symmetry of the initial state orbitals occupied by the leuchtelectrons is taken into account. The experiment selectively investigates the N_2 and O_2 double ionization channel, i.e. only events for which metastable doubly charged molecular ions reach the ion detector are considered. These ions can only be formed by double ionization in a restricted range of internuclear separations around the equilibrium point [19] thus "freezing" nuclear motion during the laser pulse.

The experimental technique is based on correlated electron and ion momentum spectroscopy [5, 20–22]. In short, ions and electrons created in the focal spot of a laser beam at the point of intersection with a supersonic molecular beam are extracted by a weak electric field ($1 - 7\,\mathrm{V/cm}$). Electrons are guided by a suitably chosen homogeneous magnetic field ($\approx 10 - 20\,\mathrm{Gauss}$) parallel to the electric field. After passage of acceleration and field-free drift tubes, the charged particles hit position-sensitive microchannel-plate detectors (diameter 80 mm) equipped with delay line anodes for position encoding. The measured time-of-flight of each particle together with the position where it strikes the detector allows the reconstruction of its complete initial momentum vector. The solid angle of detection is 4π for ions and electrons.

Correlated detection of ions and electrons is only possible if the probability for an ionization event – may it be single or double – is small (≈ 0.1) per laser shot. Together with the small yield ratio for double to single ionization ($\approx 10^{-3}$ for O_2 and $\approx 5 \times 10^{-3}$ for N_2 [23]) this means that an event of interest can be detected only every 10000th laser shot in the mean. This calls for a laser system with the highest possible pulse repetition rate while being sufficiently powerful to provide the necessary intensity for NSDI. Our laser system delivers 35 fs-pulses (FWHM) with an energy up to $6\,\mu\mathrm{J/pulse}$ at a central wavelength of 800 nm [24]. The repetition rate is 100 kHz which is unique in this type of experiment. The laser beam is focused by a parabolic mirror ($f = 80\,\mathrm{mm}$) on the atomic beam which has a width of $50\,\mu\mathrm{m}$ along the propagation direction of the laser beam. This gives rise to an interaction volume of $\approx 2 \times 10^{-9}\,\mathrm{cm}^3$. The background gas pressure is kept below $3 \times 10^{-10}\,\mathrm{mbar}$.

The sum-momentum distribution of the two photoelectrons for the momentum component parallel to the direction of linear laser beam polarization is considered to provide most obviously an indication of the mechanism of NSDI. Fig. 1 shows this distribution (solid lines) for N_2 at $1.5 \times 10^{14}\,\mathrm{W/cm^2}$ (a), and for O_2 at $1.1 \times 10^{14}\,\mathrm{W/cm^2}$ (b) and at $1.7 \times 10^{14}\,\mathrm{W/cm^2}$ (c). The laser intensities were chosen in a regime where NSDI has been reported to dominate [9, 10]. Both, N_2 as well as O_2 do not show the double hump structure considered to be chracteristic for NSDI due to recollision. Most clearly this double hump structure in the sum-momentum distributions has been found for Ne [5]. However, also in the present case the "cutoff" [22] for the N_2 distribution is located close to $\pm 4\sqrt{U_p}$ as expected for instantaneous impact ionization of N_2^+ via electron recollision [22] (Fig. 1a). U_p denotes the ponderomotive energy, i.e. the quiver energy of an electron in the laser field. Moreover, the correlation of the final state electron momentum components parallel to the laser beam polarization vector in Fig. 2a clearly shows the characteristics expected for recollision double ionization of N_2. Similar to the atomic case the two photoelectrons are emitted preferentially with similar momentum components $\left(p_{i,||},\, i = 1, 2\right)$ into the same half space [6, 7, 22, 25]. However, differences do exist between N_2 and the atoms Ar and Ne. For N_2 a large amount of electron pairs is found with small $p_{i,||}$ for both of them. These are responsible for the missing double hump structure in the projected electron sum-momentum distribution in Fig. 1a. Nevertheless, the N_2 data are compatible with NSDI due to recollision.

In contrast, the O_2 sum-momentum distributions (Fig. 1b,c) are much narrower than that for N_2 (Fig. 1a), even though the light intensity is higher in Fig. 1c. The expected "cutoff" momentum $4\sqrt{U_p}$ is clearly too large. Rather, the observed "cutoff" is better described by $\pm 2\sqrt{U_p}$. The momentum correlation of the photoelectron pairs in Fig. 2b also does not show the characteristics expected for impact ionization in a recollision event. This suggests the conclusion that double ionization of O_2 proceeds sequentially. In order to test this, we calculated sum-momentum distributions to be expected for this scenario with a semi-classical model. Quasistatic electric field ionization is assumed for both ionization steps. The symmetry of the initial state orbitals occupied by the O_2 and O_2^+ leuchtelectrons is included in the calculation, however in a simplified way [27]. Further on, averaging over the randomly oriented internuclear axis was performed. This is necessary because the short light pulses do not align the molecules. The result of the calculation is shown in Fig. 1b,c. Obviously, the theoretical curve is narrower than the experimental one. The result is even more significant as

our theoretical model overestimates the width of the momentum distribution. The latter can be concluded from the comparison of the respective experimental and theoretical results for single ionization. The coercible conclusion is that double ionization proceeds *not* sequentially also for O_2, i.e. NSDI does exist also for this molecule.

The question however remains, whether recollision is still the underlying mechanism for NSDI of O_2. We address this question by assuming that this *is* the case and compare the experimental data with the results of a theoretical model which includes recollision as well as the symmetry of the initial state of the molecule. In particular, the model should be able to reproduce the completely different sum-momentum distributions and final state electron momentum correlations for O_2 and N_2. The calculation is based on a classical analog of the quantum mechanical S-matrix for recollision double ionization [28]. According to this the differential probability for double ionization $|S(\mathbf{p}_1, \mathbf{p}_2)|^2$ is proportional to a form factor [29]. The form factor here is factorized into a contribution $g_1(\mathbf{k})$ describing the transition of the first electron to the continuum, and another contribution $g_2(\mathbf{p}_1, \mathbf{p}_2, \mathbf{k})$ describing the inelastic recollision. $\mathbf{p}_1$ and $\mathbf{p}_2$ are the final state momenta of the electrons and $\mathbf{k}$ is the intermediate state momentum of the recolliding electron.

The inelastic scattering matrix element g_2 is calculated in Born approximation with the wavefunction of the bound electron constructed by the method of linear combination of atomic orbitals (LCAO). For the latter the bound state of a δ-potential is used (for justification see [29]). As a consequence, the orbital is either of σ_g or σ_u type. Although the O_2 orbital is not a σ_u one, it nevertheless reflects the initial state symmetry thus allowing to test the hypothesis that the symmetry of the initially occupied orbital is decisive. The electron-electron interaction which mediates the transition is assumed to be a contact interaction. With these approximations g_2 reads explicitly

$$g_{2,\pm} = \frac{h_{2,\pm}(|\mathbf{R}|)}{2\,|E_2| + (\mathbf{k} - \mathbf{p}_1 - \mathbf{p}_2)^2} \begin{cases} \cos\frac{(\mathbf{k}-\mathbf{p}_1-\mathbf{p}_2)\cdot\mathbf{R}}{2} & (+) \\ \sin\frac{(\mathbf{k}-\mathbf{p}_1-\mathbf{p}_2)\cdot\mathbf{R}}{2} & (-) \end{cases} \tag{1}$$

where $h_{2,\pm}$ is a function of the internuclear separation $|\mathbf{R}|$. It is not relevant for the further discussion. $|E_2|$ is the time dependent ionization potential of the singly charged ion [22].

The transition matrix element of the first electron to the continuum is split into a rate part and into g_1, a geometry part, which is incorporated in the form factor. The orbital initially occupied by the electron is again constructed using the LCAO method as above and,

consequently, a contact electron-ion interaction is used. g_1 then appears as an intermediate state interference term

$$g_{1,\pm} = h_{1,\pm}(|\mathbf{R}|) \begin{cases} \cos\frac{\mathbf{k}\cdot\mathbf{R}}{2} & (+) \\ \sin\frac{\mathbf{k}\cdot\mathbf{R}}{2} & (-) \end{cases} \tag{2}$$

In equations (1) and (2) the (+) is for the σ_g and the (−) for the σ_u initially occupied orbital. In terms of g_1 and g_2 the model form factor reads $|V_{\mathbf{p}_1,\,\mathbf{p}_2,\,\mathbf{k}}|^2 = |g_1(\mathbf{k})\, g_2(\mathbf{p}_1,\, \mathbf{p}_2,\, \mathbf{k})|^2$. Again we average over the random orientation of the internuclear axis.

The calculated electron momentum correlation for $p_{i,||}$, $i = 1, 2$ is shown in Fig. 3a for N_2 at $1.5 \times 10^{14}\,\mathrm{W/cm^2}$ and in Fig. 3b for O_2 at $1.7 \times 10^{14}\,\mathrm{W/cm^2}$. The calculation for N_2 shows an electron momentum correlation that is clearly different from that for Ar at a similar light intensity [22]. In fact, we find a correlation similar to that observed in the experiment with a significant amount of events appearing where both electrons have small and similar $p_{i,||}$, $i = 1, 2$. The calculation also indicates that the specific shape of the distribution is mainly determined by final state interference via the matrix element $g_{2,+}$. Changing $g_{1,+}$ (e.g. using its atomic value 1) has only little effect. The reason for this behavior is that $\mathbf{k}\,\mathbf{R}/2 < \pi/2$ (with $\mathbf{k} = -\mathbf{A}\,(t')\,/c$ in our model, t': transition time of the first electron to the continuum) where the first zero of $g_{1,+}$ appears. An increasing influence of $g_{1,+}(\mathbf{k})$, is expected at light intensities where $\mathbf{k}\,\mathbf{R}/2 > \pi/2$.

For O_2 a significantly different correlation is found (Fig. 3b). In spite of the slightly higher light intensity it is concentrated near $p_{1,||} = p_{2,||} = 0$. This again is similar to what is found in the experiment (Fig. 2b) together with a correspondingly narrow electron sum-momentum distribution (Fig. 1c). Due to the approximations made, a full quantitative agreement between experiment and model calculation is not expected. At the lowest light intensity investigated ($1.1 \times 10^{14}\,\mathrm{W/cm^2}$, Fig. 1b) also the qualitative agreement is lost. In contrast to the experiment the calculated electron momentum correlation develops a separated double hump structure. This discrepancy probably has its origin in the classical approach of our model. The classically accessible phase space where $E_{kin}\,(t) \geq |E_2\,(t)|$ [22] gets very small near $p_{i,||} = 0$. Quantum mechanics may increase the probability to find electron pairs with small $p_{i,||}$ thus filling in the hole in the classical model distribution function.

The origin of the localized electron momentum correlation for O_2 (Fig. 3b) is found in $g_{1,-}$. The sine term suppresses recollision of electrons with small $\mathbf{k}$. They are field ionized

near the extrema of the oscillating electric field of the light wave. This in turn leads to an efficient suppression of final state electrons with large $p_{i,||}$ for both of them. At low light intensity the influence of this term is found to be reduced significantly. Different from N_2 the initial state symmetry thus comes in mainly via $g_{1,-}$.

In conclusion, we provided evidence for NSDI in N_2 and O_2 by momentum spectroscopy. The main features found can be understood within the framework of the recollision model with direct electron impact ionization of the singly charged molecular ion. Molecular structure influences the electron momentum correlation decisively. In fact, the structure, including the initial state symmetry, appears to be more important than for single ionization. For N_2 the molecular structure arises in the inelastic recollision event and gives rise to distinct differences between N_2 and Ar correlation spectra. On the other hand, the concentration of the momentum correlation spectrum near $p_{1,||} = p_{2,||} = 0$ for O_2 is mainly determined by the symmetry of the orbital occupied by the molecular leuchtelectron. The main influence of molecular structure is found in the electron sum-momentum (along the main diagonal in Figs. 2 and 3). The effect on the difference-momentum (along the minor diagonal in Figs. 2 and 3) is less pronounced. Averaging over statistically oriented molecular axes in the experiment and calculation washes out much of the interference due to molecular structure. The model calculation shows that aligning the axis with respect to the laser polarization vector should give rise to a much more pronounced effect.

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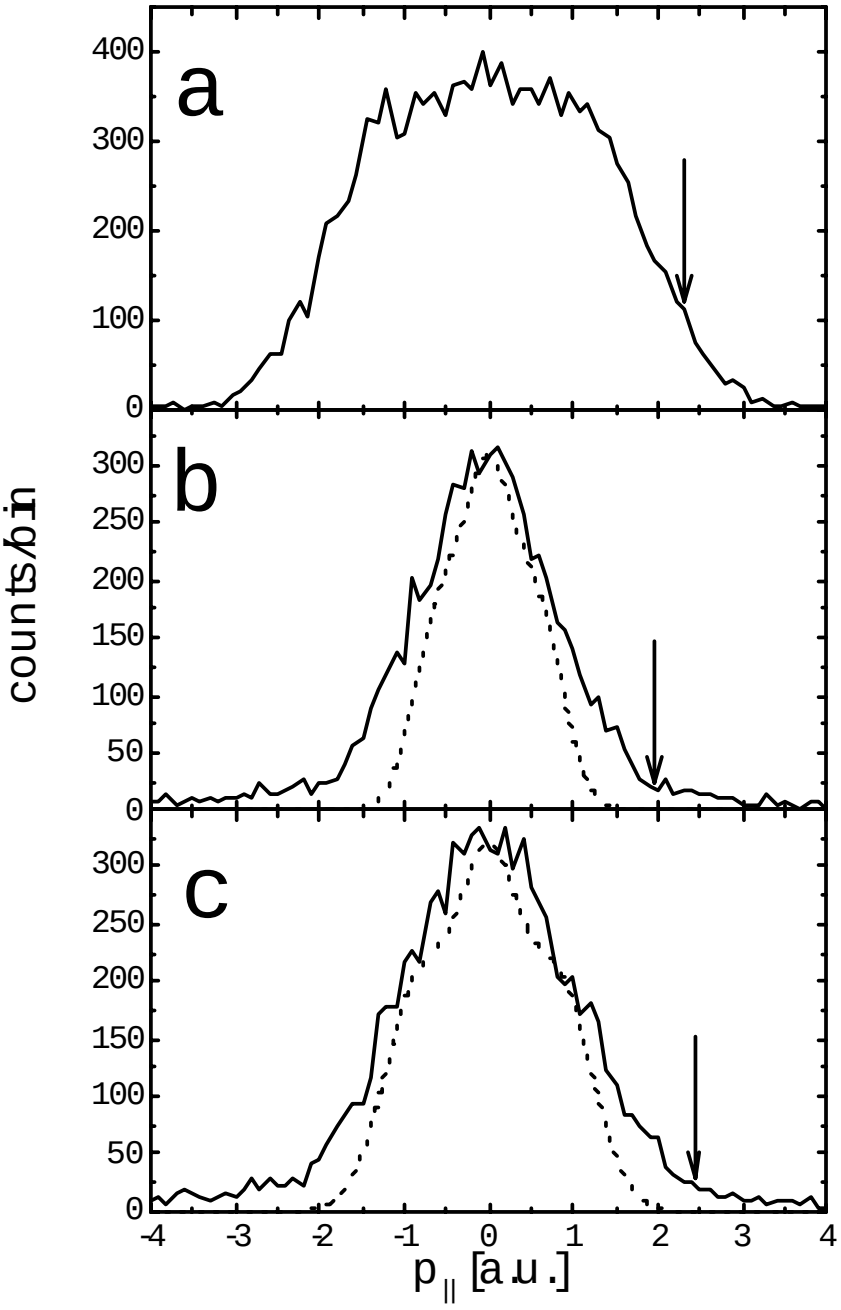

FIG. 1: Measured electron sum-momentum distributions (full lines) after double ionization of (a) N_2 at $1.5 \times 10^{14}\,\mathrm{W/cm^2}$, (b) O_2 at $1.1 \times 10^{14}\,\mathrm{W/cm^2}$, and (c) O_2 at $1.7 \times 10^{14}\,\mathrm{W/cm^2}$. The distributions are shown projected on an axis parallel to the laser beam polarization vector. The arrows indicate the "cutoff" momentum of $4\sqrt{U_p}$ which is expected for NSDI due to recollision. For O_2 the dotted lines show calculated spectra if sequential double ionization is assumed.

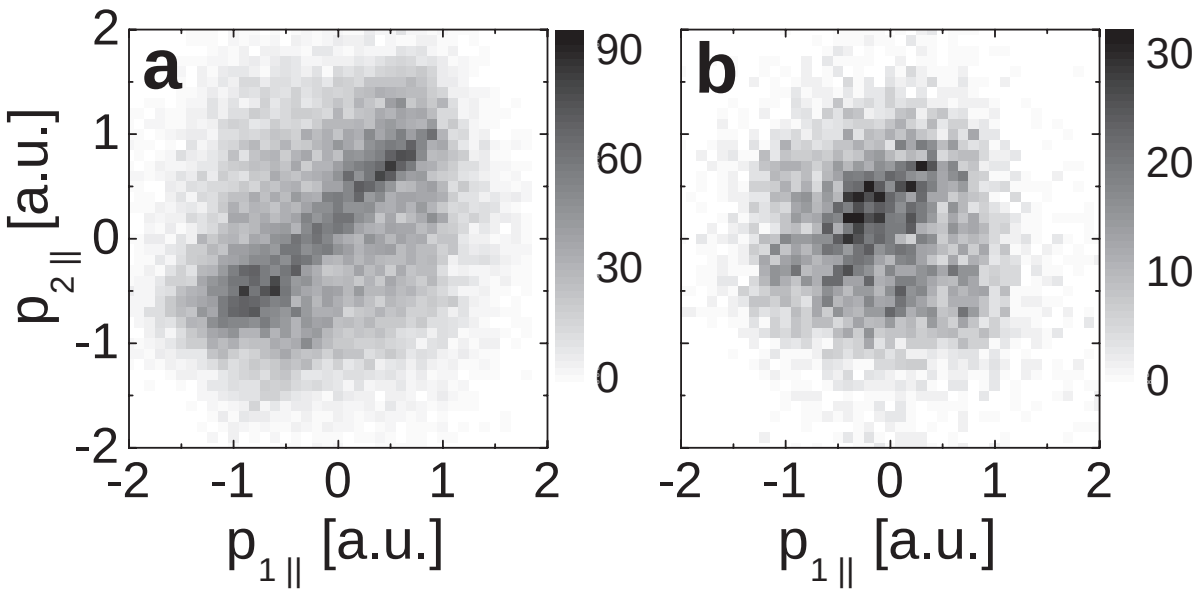

FIG. 2: The electron momentum correlation for the momentum components parallel to the light beam polarization vector: (a) N_2 at $1.5 \times 10^{14}\,\mathrm{W/cm^2}$ and (b) O_2 at $1.7 \times 10^{14}\,\mathrm{W/cm^2}$.

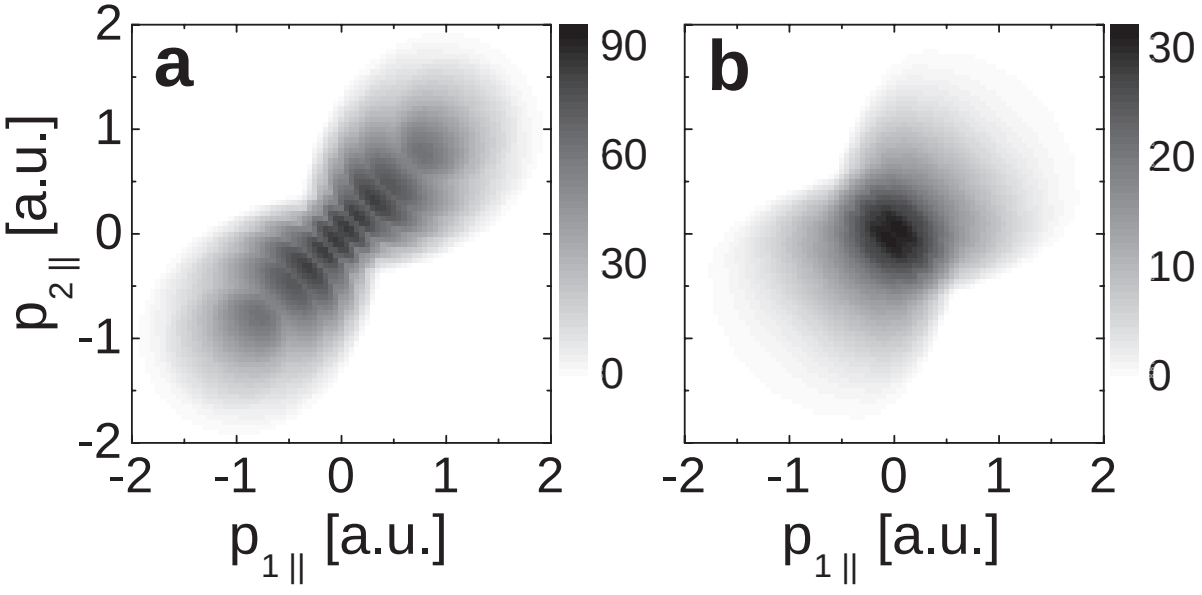

FIG. 3: Calculated electron momentum correlation for N_2 (a) and O_2 (b). The light intensities are chosen as in Fig. 2.