

Effects Of Molecular Structure on Ion Disintegration Patterns In Ionization of O₂ and N₂ by Short Laser Pulses

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We demonstrate that the structure of the outermost orbitals of oxygen and nitrogen can be observed in the angular distribution of coincident ion pairs generated by the double ionization of these molecules by 8 fs laser pulses. We do this by establishing that these ions emerge from well defined excited electronic states of O₂²⁺ and N₂²⁺ respectively and that they are produced dominantly through a process which involves electron rescattering. The angular distributions of the ions from the two targets are very different, reflecting the different structures of the outermost orbitals of the two molecules.

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When a single electron is removed from a molecule by a fast laser pulse, does the ionization rate depend on the relative alignment of field and molecule? This question has arisen often, most recently in connection with the puzzle of ionization suppression. For certain molecules, such as O₂ and S₂, for example, it has been observed that ionization rates are suppressed relative to atoms with nearly equal ionization potentials [1–6]. Molecules with suppressed ionization also display an extended spectrum of harmonics, indicating that they hold together longer in the laser field than might be expected simply on the basis of their ionization potentials [7]. Several models have been proposed to explain this [7–12]. A recurring theme in the explanations is that the structure of the wave function of the outermost orbital of the molecule plays a crucial role in determining the ionization probability [8,11,12]. The symmetry of the outermost orbital of N₂ is a 3σ_g, while that of the O₂ is a π_g. The ionization rate can depend on this symmetry through a destructive interference between electron emission amplitudes from the two centers of the molecule [11,12]. In a different but related formulation by Tong *et al.* [13], the commonly used Ammosov-Delone-Krainov (ADK) tunneling model [14] was extended to take into account the asymptotic form of the orbital from which the electron is being removed.

In this Letter, we use the angular distributions of coincident ion fragments to seek evidence for the influence of the structure of the outermost orbitals on the dependence of the double ionization rate on the angle θ between the molecule and the polarization vector. We find the previously undocumented result that this process proceeds through well defined and identifiable states of the excited dications, and that the N₂ ions are much more likely to be emitted when the molecule is aligned along the polarization vector, while the O₂ ions prefer that the molecule be at some angle to the electric field. We inter-

pret this effect in terms of the molecular ADK model [13].

For the low intensity pulses used here we believe that the mechanism for doubly ionizing these molecules is that shown schematically in Fig. 1. The steps are similar to those recently seen and modeled for the rescattering double ionization of H₂ [15–19]. The first step is the removal of the outermost electron from the molecule through tunneling ionization (TI). According to the molecular ADK model, the angular distribution for this step, $P_1(\theta)$, will maximize strongly at $\theta = 0^\circ$ for the 3σ_g orbital of N₂, and at about 40° to the field for the π_g orbital of O₂. The second step is the rescattering excitation of the singly charged molecule, for which the angular distribution, $P_2(\theta)$ is likely to have a weaker angular

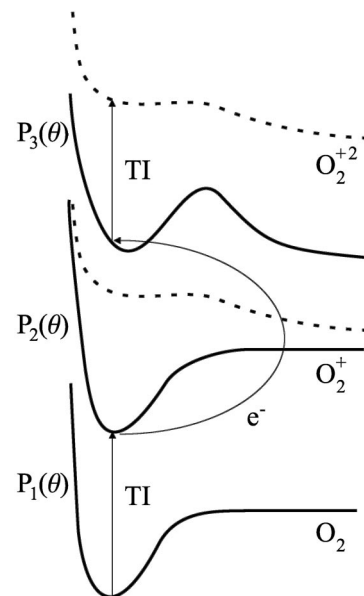


FIG. 1. Schematic of double ionization processes.

dependence because electron excitation cross sections are likely to be much less demanding of angular alignment than field ionization [17–19]. The final step is the removal of the other outermost electron from the singly charged molecule, with angular dependence $P_3(\theta)$, reaching an excited state of the dication. An excited electronic state of this ion must be reached to make a dissociating molecule: removal of the two outermost electrons from either neutral molecule will only make a metastable dication whose alignment cannot be determined using the method of this paper.

Our experimental approach is to measure the full momentum vectors of coincident pairs of O^+ or N^+ ions produced by 8 fs pulses with laser powers below 2×10^{14} W/cm² from a jet target of the molecular gas. We use a cold target recoil ion momentum spectroscopy arrangement which has been described in Refs. [20,21]. We use a rectangular coordinate system with the laser propagating in the z direction, polarized along x and with the jet velocity along y . Ions produced in the laser focus were projected by a static electric field of 30 V/cm onto the face of a position- and time-sensitive channel-plate detector 5.3 cm away. The position and arrival time of both ions were recorded on an event-by-event basis and the original momentum vectors of the coincident singly

charged ions were calculated. Many charge state combinations and ions appear in our spectra; we choose here to select only the O^+/O^+ or N^+/N^+ channel.

Figure 2 shows xz slices of the momentum spheres obtained for the two molecules. These were obtained by requiring that the y component of momentum not exceed 30 a.u. We notice immediately, especially in the oxygen spectrum, that distinct rings are seen. These correspond to the dissociation of the molecule through well defined states of the dications. Figure 3 shows the corresponding one-dimensional kinetic energy release (KER) spectra obtained by collapsing the momentum spheres into the energy release axis. The states populated can be identified (see Table I) as those observed by Lundquist *et al.* [22,23] for electron bombardment of the same targets. A similar identification was suggested for nitrogen by Nibarger *et al.* [24], who, however, did not have the necessary resolution to resolve individual electronic states. It is immediately clear that the widespread use of “Coulomb” potentials to describe such a dissociation is inappropriate.

At these intensities, the production of ion pairs was observed to be reduced by more than an order of magnitude by circularly polarizing the radiation, keeping the peak field constant. This result is to be expected also from previous measurements on these and similar molecules [25–27], and we interpret this to mean that the production of the ion pairs requires that a rescattering event be present. Circularly polarizing the laser prevents an electron emitted in step one from returning to the molecule,

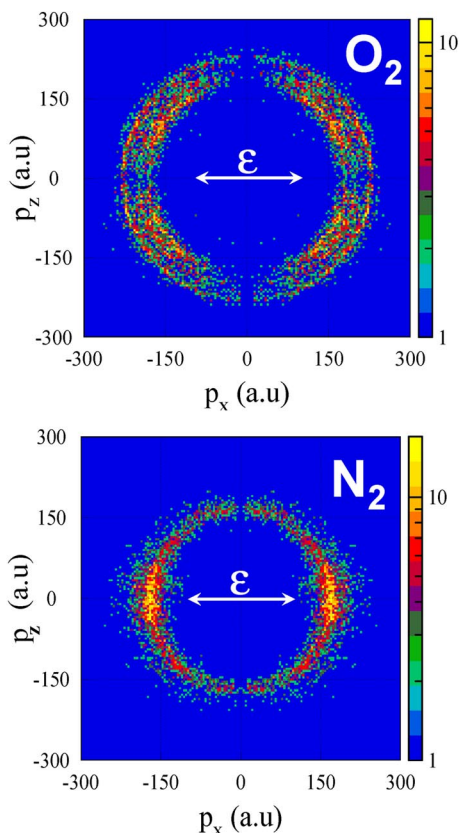


FIG. 2 (color online). Slices in the xz plane of the momentum sphere showing the dissociation of molecules into two singly charged ions O_2 (upper panel) and N_2 (lower panel).

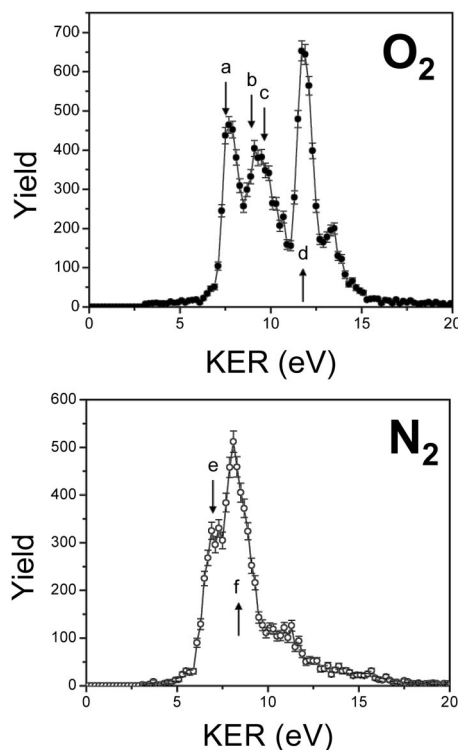


FIG. 3. Kinetic energy release spectra for O_2 (upper panel) and N_2 (lower panel).

TABLE I. Electronic states of the dications whose decay we observe. Adapted from Refs. [22,23]. Configurations are indicated relative to the ground state configurations of the neutral molecule, which are O_2 ($..3\sigma_g^2 1\pi_u^4 1\pi_g^2$) $3\Sigma_g^-$ and N_2 ($... \pi_g^4 3\sigma_g^2$) $1\Sigma_g^+$.

State	Major conf.	KER(eV)	Final State	Figure3
O_2^{2+}				
$W^3\Delta_u$	$\pi_u^{-1} 1\pi_g^{-1}$	7.2	$O^+(^4S) + O^+(^2D)$	a
$B^3\Sigma_u^-$	$\pi_u^{-1} 1\pi_g^{-1}$	8.4	$O^+(^4S) + O^+(^2D)$	b
$1^1\Delta_u$	$\pi_u^{-1} 1\pi_g^{-1}$	8.9	$O^+(^4S) + O^+(^2D)$	c
$1^1\Sigma_u^+$	$\pi_u^{-1} 1\pi_g^{-1}$	9.7	$O^+(^4S) + O^+(^2D)$	d
$B^3\Pi_g$	$3\sigma_g^{-1} 1\pi_g^{-1}$	11.2	$O^+(^4S) + O^+(S)$	d
$1^1\Pi_g$	$3\sigma_g^{-1} 1\pi_g^{-1}$	12.7	$O^+(^4S) + O^+(S)$	d
N_2^{2+}				
$A^1\Pi_u$	$\pi_u^{-1} 3\sigma_g^{-1}$	6.9	$N^+(^3P) + N^+(^3P)$	e
$d^1\Sigma_g^+$	$\pi_u^{-2} 3\sigma_g^{-0}$	8.6	$N^+(^3P) + N^+(^3P)$	f
$D^3\Pi_g$	$\pi_u^{-2} 3\sigma_g^{-1} \pi_g^1$	8.0	$N^+(^3P) + N^+(^3P)$	

thereby cutting off the rescattering step [15–19]. We mention that at higher laser intensities, above about 5×10^{14} W/cm², this behavior changes completely: one then enters a sequential ionization region where circularly polarizing the light has little effect on the yield or the KER spectrum.

The different angular distributions for N_2 and O_2 are shown in polar plots in Fig. 4. The N_2^+ is strongly peaked along the laser vector, while the O_2 for most of the peaks in the KER spectra show a tendency to maximize closer to 40° , with a clear tendency to actually decrease at 0° .

We interpret the angular dependence as due to the first step in Fig. 1. Figure 5 shows theoretical angular distributions of the single ionization rate calculated using the molecular ADK [13] for the outer orbitals of O_2 and N_2 , which are π_g and $3\sigma_g$, respectively. These angular distributions reflect directly the asymptotic structure of these orbitals, shown schematically in the right hand panel of Fig. 5. It is remarkable that the peaking of the O_2 distribution is as close as it is to the predicted maximum of $P_1(\theta)$ at 40° , since the observed distribution should not be due to this step alone but to the folding together of the angular dependences of all three steps. We attribute this to the weak angular dependence of $P_2(\theta)$ and from the expected near isotropy $P_3(\theta)$, since this last step is likely to be well into saturation for the outermost electron.

One might ask whether the laser field itself aligns the molecules before the ionization processes discussed here occur. Although one would not expect that these fields are strong enough to align the neutral molecules in less than a few hundred fs [28], there is considerable evidence that even for pulses as short as 50 fs, such an alignment may occur when dynamically excited systems are involved [29–36]. Indeed, if we use 35 fs pulses instead of 8 fs pulses at the same peak intensity, we observe patterns

similar to those shown in Fig. 4 but with the maxima in the oxygen spectra shifted toward zero degrees. We interpret this to indicate that dynamic alignment of the molecules takes place on this slightly longer time scale.

We point out that the reduction of the double ionization near 0° for oxygen might also be due to the interference of the wave packet with itself as it returns to the molecule. If a wave packet were emitted at 0° from the O_2 with the molecule aligned with the laser field, a returning wave packet with π_g symmetry would suffer destructive interference between its positive and negative parts at the convergence of its return, thus turning off rescattering [37]. We cannot exclude that this effect also plays a role here.

Thus our data appears to strongly support the interpretation that sequential ionization, involving a rescattering process, is involved in doubly ionizing these molecules at these intensities, and that the π_g structure of the O_2 molecule is at the root of the exceptional resistance of this molecule to ionization. This result is in good agreement with conclusions recently reached by Eremina *et al.* [38] on the basis of electron spectra, and with those of Litvinyuk *et al.* [39] who used rotational wave packets to align N_2 (but were not able to do so with O_2). They are also consistent with recent harmonic generation experiments of Légaré *et al.* [40], who find that harmonic generation from O_2 is favored when the molecule is aligned away

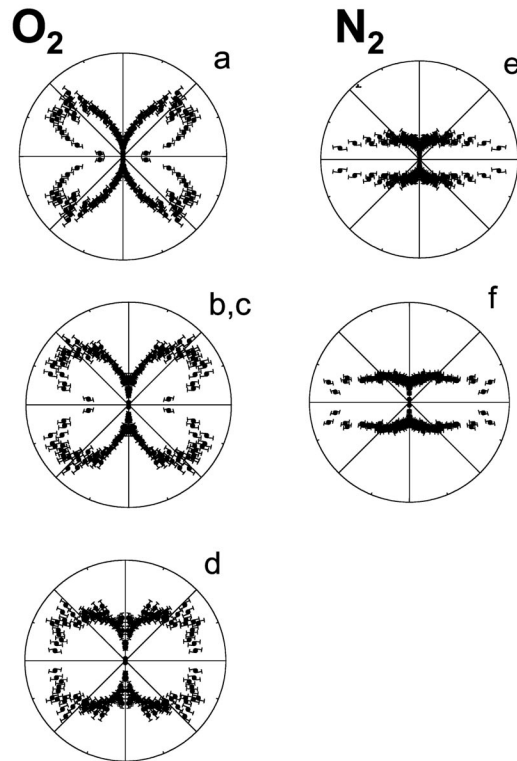


FIG. 4. Polar plots of the experimental angular distributions for different decay channels for O_2 (left) and N_2 (right).

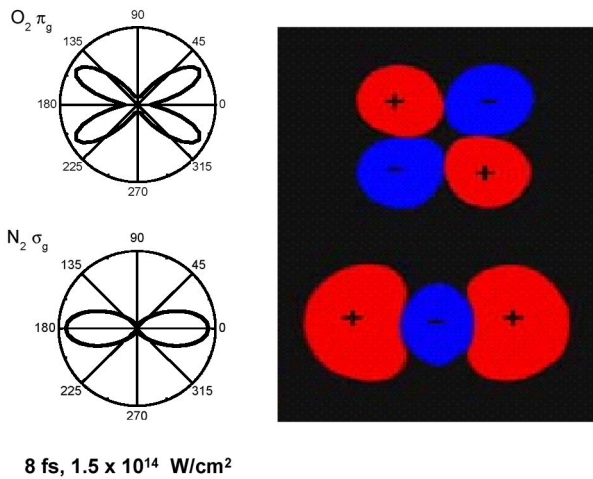


FIG. 5 (color online). Polar plots of the theoretical angular distributions expected for the removal of the outermost electron from O₂ (upper panel) and N₂ (lower panel). The schematic at the right shows the orbital structures of these orbitals.

from the polarization vector. It would be of great interest to extend these experimental studies to other molecules with π_g outer orbital, such as F₂, for which ionization suppression is not observed.

Finally we note that the B³Π_g state (stated in Fig. 3 and Table I) of oxygen tends not to show the 40° maximization, but rather maximizes near 0°. This state has a large component of the configuration $3\sigma_g^{-1}1\pi_g^{-1}$ [22,41], while the states with KER below 10 eV (a-c) observed are primarily $1\pi_u^{-1}1\pi_g^{-1}$, where the reference “vacuum” state is the neutral oxygen molecule. We suspect that this anomalous behavior may be due to the extraction of an (inner) $3\sigma_g$ electron [42] rather than the (outer) one π_g electron in the first step, which would give rise to a peaking at 0°.

In summary, we have established that, for a peak laser intensity at or below 2×10^{14} W/cm², the removal of two electrons from O₂ and N₂ proceeds through a nonsequential process requiring a rescattering event, and through well defined and identifiable states of the dication of these species. The angular distributions of the ions strongly suggest that the mechanism is the very anisotropic removal of one electron, followed by a rescattering and a subsequent laser ionization of the excited singly charged molecule. The angular distributions show the behavior expected from the symmetries of the $1\pi_g$ outer orbital for O₂, and the $3\sigma_g$ orbital for N₂. There remains, however, a puzzle associated with the production of the dication of oxygen with a $3\sigma_g$ hole.

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