Alignment-Dependent Strong Field Ionization of Molecules

I. V. Litvinyuk,[1] Kevin F. Lee,[1,2] P. W. Dooley,[1,2] D. M. Rayner,[1] D. M. Villeneuve,[1] and P. B. Corkum[1,2]

[1]*Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, K1A 0R6, Canada*
[2]*Department of Physics & Astronomy, McMaster University, 1280 Main Street West, Hamilton, Ontario, K1S 5P3, Canada*
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We demonstrate a method to measure strong field laser ionization of aligned molecules. The method employs a macroscopic field-free dynamic alignment, which occurs during revivals of rotational wave packets produced by a femtosecond laser pulse. We investigate the dependence of strong field ionization of N_2 on molecular orientation. We determine that N_2 molecules are four times more likely to ionize when aligned parallel to the field than when aligned perpendicular to it.

Experiments on gas phase molecules are generally performed on samples with an isotropic distribution of molecular orientations. In many cases, angular averaging imposes a severe limitation on the information that can be extracted from the experimental data. For example, theoretical models suggest that the strong field ionization rate for neutral molecules depends on the molecular orientation with respect to the laser field [1–3]. However, there have been no reports of any experimental studies verifying the theoretical predictions.

Angle dependent ionization rates are important for understanding strong field molecular physics. For example, the angle dependent ionization affects the high harmonics yields with parallel and perpendicular molecules [4,5]. Interpretation of these experiments will be difficult until the angle dependent ionization rate is accurately known. In addition, the apparent suppression of ionization for some molecules [6] was explained by destructive interference of electron wave packets propagating along certain directions due to the symmetry of the molecular orbitals [7]. Measurements of angle dependent ionization rates will provide a definitive test for such models.

Experiments have recently shown that molecules can be aligned by strong, low frequency, nonresonant laser pulses [8–10]. If the laser pulse is long, the molecule can be adiabatically trapped [8,10] in pendular states [11]. If the laser pulse is either short [10,12–14], or rapidly truncated [15,16], rotational wave packets are produced. For linear molecules the wave packets formed in the latter case yield macroscopic dynamic alignment at well-defined revival times following the rapid transient.

The main purpose of our Letter is to demonstrate a method for measuring the alignment dependence of the strong field molecular single ionization probability. The method does not rely on rapid dissociation of the molecule following ionization. We show that at an ionizing laser intensity of 2×10^{14} W/cm^2 N_2 molecules aligned parallel to the field are ~4 times more likely to ionize than molecules oriented perpendicular to it.

The method employs a macroscopic field-free dynamic alignment, which occurs during revivals of rotational wave packets produced by a femtosecond laser pulse. A short, linearly polarized pump (aligning) pulse produces a rotational wave packet. A much more intense, circularly polarized probe (exploding) pulse measures the time-dependent angular distributions of molecular axes by Coulomb exploding the molecules. The exploding pulse produces highly charged N_2 ions, which undergo immediate, directed dissociation (Coulomb explosion) into atomic ion fragments. A much weaker linearly polarized probe pulse is then used for studying alignment-dependent single ionization of N_2 molecules.

The use of a circularly polarized probe pulse for measuring time-dependent angular distributions is important to eliminate the bias introduced by the anisotropy of the Coulomb explosion process [17]. This process is highly directional and is most efficient for molecules aligned parallel to the laser field [18–20]. The polarization axis of the (linear) aligning pulse lies in the polarization plane of the (circular) exploding pulse. We measure the angle, ϑ, between the alignment axis and the projection of each three-dimensional fragment velocity onto the polarization plane. Since the exploding pulse is circularly polarized, Coulomb explosion is independent of the angle ϑ. Hence, experimental ϑ distributions are unbiased and depend solely upon the actual distribution of molecular orientations.

To characterize the degree of alignment at each pump-probe delay, we calculated $\langle \cos^2 \vartheta \rangle$ for each ϑ distribution. In our scheme, $\langle \cos^2 \vartheta \rangle = 0.5$ corresponds to an isotropic distribution of molecular orientations, while $\langle \cos^2 \vartheta \rangle = 1$ represents complete alignment along the polarization axis.

Laser pulses (800 nm, 40 fs, 500 Hz repetition rate) from a Ti:sapphire regenerative amplifier were split in two by an interferometer. The linearly polarized aligning pulse passed through a telescope, which decreased its diameter by a factor of 2. This has two advantages. First, the subsequent focal volume is increased such that

the probe pulse focuses entirely within it. Second, the peak focal intensity is decreased to keep the aligning pulse intensity sufficiently low to avoid ionization. The probe pulse passed through a variable delay line and a quarter wave plate used to produce either circular or linear polarization. The two beams were recombined collinearly and focused by an on-axis parabolic mirror into a collimated beam of nitrogen molecules.

The molecular beam had a cross section of 40 mm (along the laser propagation direction) by 1.5 mm and a density of $\sim 10^{10}$ molecules/cm^3. The measured longitudinal translational temperature of the molecular beam was 90 K. We expect the rotational temperature to be similar. The beam temperature in the transverse direction is dictated by geometric constraints and was measured to be less than 0.01 K.

Coulomb explosion fragments were analyzed using a uniform electric field, imaging mass spectrometer. Molecular fragments were detected using a helical delay-line anode time- and position-sensitive detector. From the ion impact data, the complete velocity vector for each Coulomb explosion fragment (and hence the orientation of the molecule from which it originated) was determined.

Before turning to the experimental results, we describe a new method for accurate measurement of laser intensity. The transverse temperature of the molecular beam ($\sim 10^{-7}$ eV) is negligible in comparison to the ion recoil kinetic energy from strong field ionization ($\sim 10^{-3}$ eV). Therefore, a measurement of the ion recoil momentum resulting from ionization by circularly polarized light determines the laser intensity at which the ion is produced.

In circularly polarized light, an ion acquires drift velocity [21], ν_∞, such that

$$\frac{1}{2} m \nu_\infty^2 = \frac{q^2 E_0^2}{2m\omega^2}, \tag{1}$$

where ν_∞ is the experimentally determined ion drift velocity, q and m are the ion charge and mass, respectively, E_0 is the electric field amplitude, and ω is the angular frequency of the laser. Having determined E_0, the intensity can be immediately obtained as $I = \varepsilon_0 c E_0^2$ (circular polarization), where ε_0 is the permittivity of vacuum and c is the velocity of light. This determines the maximum intensity at which ions are produced. Below ionization saturation this intensity equals the peak laser intensity. We believe this to be a simple, yet accurate ($\pm 10\%$) method of measuring the laser intensity *in situ*.

Having established the laser intensity corresponding to specific pulse energy, we scaled the other intensities according to that value. The intensity of the aligning pulse was 5×10^{13} W/cm^2. The intensity of the probe pulse was 4×10^{15} W/cm^2 for Coulomb explosion, and 2×10^{14} W/cm^2 for single ionization.

In the alignment experiments, Coulomb explosion was used for molecular angle determination. Because a highly charged N_2 parent ion dissociates before significant molecular reorientation occurs, the asymptotic fragment velocities are (to a good approximation) parallel to the molecular axis at the time of ionization. We analyzed N^{3+} ions originating from the asymmetric $N_2^{5+} \rightarrow N^{3+} + N^{2+}$ dissociation channel. This channel is characterized by N^{3+} ion kinetic energies in the $15-25$ eV range. For each N^{3+} ion, the total velocity vector was calculated and projected onto the polarization plane of the exploding pulse to yield the angle ϑ. As discussed above, the degree of alignment was then determined by calculating $\langle \cos^2 \vartheta \rangle$ for 2000 ions at each delay.

Figure 1 shows the time evolution of the alignment parameter $\langle \cos^2 \vartheta \rangle$. The aligning pulse transfers population to higher rotational states via a series of Raman transitions [14]. In classical terms, the pulse electric field exerts a torque on molecules leading to alignment along the polarization axis. Since the aligning pulse duration is very short, little molecular reorientation occurs during the pulse. Maximum alignment is observed after the pulse, followed by a series of periodic recurrences. The revivals of the rotational wave packet corresponding to $\frac{1}{4}$, $\frac{1}{2}, \frac{3}{4}$, and a whole fundamental rotational period are noted in the figure.

We also observe some time-independent alignment of molecules (i.e., $\langle \cos^2 \vartheta \rangle > 0.5$) between revivals. The selection rules for Raman transitions require that
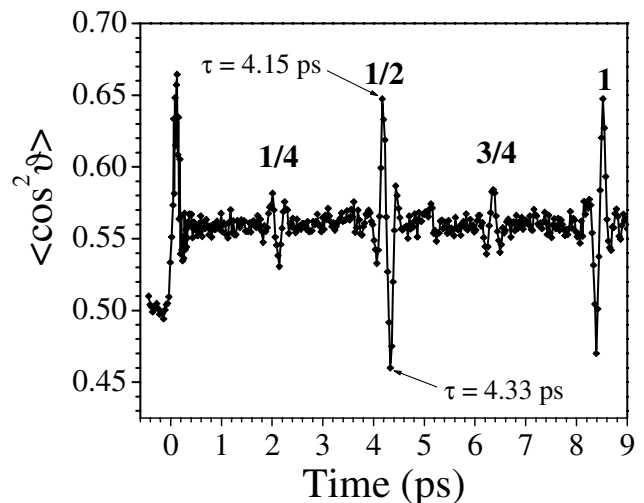

FIG. 1. Time dependence of the molecular alignment parameter $\langle \cos^2 \vartheta \rangle$ for N_2 following a 40 fs laser pulse with peak intensity 5×10^{13} W/cm^2. Fractional and full revivals are indicated on the figure. Within the first half revival, time delays corresponding to maximum alignment of molecules parallel and perpendicular to polarization of the aligning pulse are shown. ϑ is the angle between the projection of the molecular axis onto the circular polarization plane of the probe pulse and the polarization vector of the aligning pulse.

$\Delta J = \pm 2$ and $\Delta M = 0$, where J is the total angular momentum and M is its projection on polarization direction in units of $\hbar$. Because of that, the aligning pulse produces a net increase in J values while the distribution of M values is unchanged. That results in time-independent net alignment manifested in Fig. 1 as an elevated baseline value of $\langle \cos^2 \vartheta \rangle > 0.5$ for $t > 0$.

We observed up to the tenth revival (84 ps delay). Since there was no significant dephasing, many subsequent revivals could have been observed. During the first half-revival, the alignment parameter $\langle \cos^2 \vartheta \rangle$ increases to its peak value at the delay of 4.15 ps and then decreases to a minimum 180 fs later.

The experimental distributions of the angle ϑ at the delays corresponding to the maximum and minimum values of $\langle \cos^2 \vartheta \rangle$ are shown in Fig. 2. During a half-revival, the molecules first align themselves parallel to the aligning pulse polarization axis and then perpendicular to it. The maximum degree of alignment that can be achieved in this experiment is limited by the initial rotational temperature of the molecular beam and by the intensity of the aligning pulse, which must be low enough to avoid significant ionization. Nevertheless, we achieved a substantial degree of alignment with a single 40 fs laser pulse.

We used dynamic field-free alignment to investigate the dependence of the single ionization probability on molecular orientation. We performed a pump-probe experiment using the same aligning pulse as before. A probe pulse (40 fs, 2×10^{14} W/cm^2 peak intensity), linearly polarized parallel to the aligning pulse, singly ionized the molecules. We measured the total N_2^+ ion signal for two delays: $\tau = 4.15$ ps (maximum alignment along the ionizing field) and $\tau = 4.33$ ps (maximum alignment perpendicular to the field). To verify the stability of the

$\tau = 4.15$ ps $\tau = 4.33$ ps
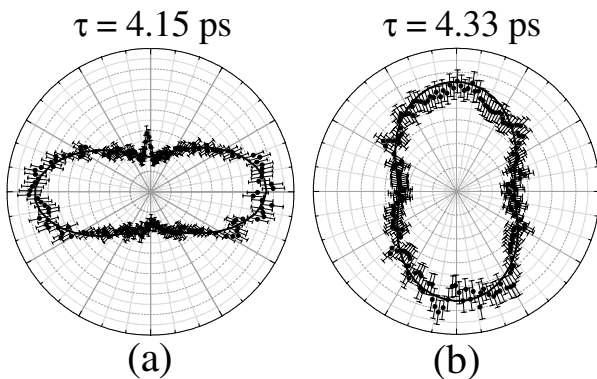
(a)   (b)

FIG. 2. Experimental angular distributions $dN(\vartheta)/d\vartheta$ for maximum alignment along the field ($\tau = 4.15$ ps) (a) and perpendicular to the field ($\tau = 4.33$ ps) (b). The polarization direction is horizontal. Solid lines represent an analytical fit to the experimental distributions by the function $F(\theta) = (\cos^2 \theta + \varepsilon^2 \sin^2 \theta)^{-1/2} + b$ with parameters $\varepsilon = 1.692$, $b = -0.415$ for (a) and $\varepsilon = 0.929$, $b = -0.916$ for (b).
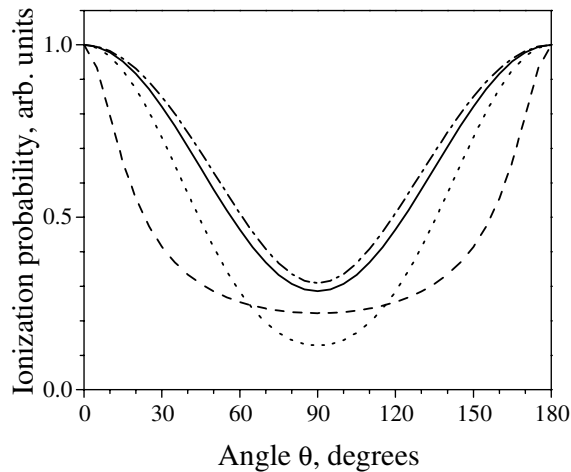
laser during the measurement, we simultaneously monitored H_2O^+ and O_2^+ ion signals that originated from background water and oxygen within the experimental chamber. Because of the different rotational constants, these molecules should not exhibit any time dependent alignment in this time range. While the water and oxygen signals were the same for both time delays, we observed that the N_2^+ signal was 1.23 times stronger for the delay corresponding to alignment along the ionizing field. Independent of any deconvolution, the N_2^+ signal enhancement clearly indicates that nitrogen molecules aligned parallel to the field are easier to ionize than those aligned perpendicular to the field.

To make a more quantitative statement regarding the relative ionization probabilities, we simulated the results using the experimentally obtained angular distributions. The total ionization signal is given by

$$S \propto \int_0^{2\pi} \int_0^\pi P(\theta, \phi) \Pi(\theta) \sin\theta \, d\theta \, d\phi, \qquad (2)$$

where $P(\theta, \phi)$ is the probability distribution for the molecular orientation with respect to the polarization axis, $\Pi(\theta)$ is the ionization probability for a molecule with its axis at an angle θ to the polarization axis, and ϕ is a polar angle about the polarization axis.

Given the cylindrical symmetry about the polarization axis of the aligning pulse, a full angular distribution of molecular orientations must exhibit the same symmetry. The full distribution can be approximated by rotating the experimental ϑ distribution about the symmetry axis, i.e., $P(\theta, \phi) = (1/2\pi)P(\vartheta)|_{\vartheta = \theta}$.

For the purpose of simulation, we must make an assumption about the functional form of $\Pi(\theta)$. Given the orbital symmetry of the nitrogen electron wave function (σ_g), it is reasonable to assume that $\Pi(\theta)$ is a monotonic function of θ in the 0–$\pi/2$ range. Two possible choices are $\Pi_1(\theta) = (\cos^2 \theta + \varepsilon^2 \sin^2 \theta)^{-1/2}$, describing an ellipsoid of rotation; and $\Pi_2(\theta) = (\varepsilon \cos^2 \theta + 1)/(\varepsilon + 1)$. The parameter ε in both functions denotes the ratio of ionization probabilities for molecules aligned parallel and perpendicular to the ionizing field.

We can calculate the ratio of total ionization signals for any two angular distributions $P_1(\theta, \phi)$ and $P_2(\theta, \phi)$ for a given function $\Pi(\theta)$, using Eq. (2). We used the experimentally measured angular distributions and optimized the parameter ε in functions Π_1 and Π_2 to obtain the experimental signal ratio. For the function Π_1 we can reproduce the experimental signal ratio with $\varepsilon = 4.5 \, (\pm 0.5)$, while the function Π_2 is best modeled using $\varepsilon = 3.5 \, (\pm 0.5)$.

It should be noted that the simulation neglects the possibility of molecular reorientation during the ionizing pulse. Since our pulse duration (40 fs) is significantly shorter than the average time taken by a nitrogen molecule to rotate by 90° (180 fs under our experimental

FIG. 3. Angular dependence of ionizaton probability. $\Pi_2(\theta) = (\varepsilon\cos^2\theta + 1)/(\varepsilon + 1)$ with $\varepsilon = 3.5$ (solid line) and $\Pi_1(\theta) = (\cos^2\theta + \varepsilon^2\sin^2\theta)^{-1/2}$ with $\varepsilon = 4.5$ (long-dashed line) best reproduce the experimental ionization data. The ionizing pulse (40 fs, 2×10^{14} W/cm^2) had the same polarization as the aligning pulse. Molecular ADK calculation for a 20 fs pulse with peak intensity of 1.6×10^{14} (short-dashed line) and 3.2×10^{14} (dash-dotted line) W/cm^2 (from Tong and Lin [22]). All curves are normalized to unity at $\theta = 0°$.

conditions), we do not believe that realignment during the pulse is critically important.

Using their molecular ADK theory [3], Tong and Lin calculated the angular dependence of the single ionization probability for nitrogen [22]. Their calculated angular dependence is well described by the function Π_2 (Fig. 3). Although done using a 20 fs pulse and intensities that differed from ours, their calculations are in good general agreement with our experimental results.

In conclusion, we have shown a general method for measuring the alignment dependence of molecular ionization. Having applied this method to N_2, we have found that the probability of ionization by a 40 fs laser pulse with peak intensity of 2×10^{14} W/cm^2 for nitrogen molecules aligned parallel to the electric field vector is ~ 4 times greater than for those aligned perpendicular to the field. This is the first direct experimental evidence of alignment dependence in strong field single ionization of neutral molecules.

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