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Field-free permanent alignment of ionized nitrogen molecules

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Abstract. Ionization occurs when strong femtosecond laser pulses propagate in nitrogen gas. The ionized nitrogen molecules are in ground electronic state as well as excited electronic states. In this paper, we study the polarization distribution of the fluorescence emission correspoding to the transition of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$). It is found that the fluorescence polarization exihibits an anisotropic angular distribution relative to the pump laser polarization, which can be attributed to the permanent alignment caused by angular-dependent ionization of neutral nitrogen molecules in strong femtosecond laser fields. The permanent alignment charactireizd by $\langle\cos^2\theta\rangle$ reaches 3/7 in our experiment where θ is the angle between the molecular axis and the pump laser polarization.

1. Introduction

When strong femtosecond laser pulses propagate in gas molecules, it would excite molecular rotational wavepackets and induce transient molecular alignment [1,2]. The alignment will be revived after the laser pulse and is called field-free alignment. The field-free molecular alignment has attracted a lot of attention and has been widely used in studying molecular dynamics in the molecular frame [3,4]. The rotational wavepacket consists of a serials of rotational states $|J, M\rangle$, where J and M are quantum numbers related to the rotational angular momentum of molecules. Because the absolute value of M is much smaller than that of J, a permanent alignment is always accompanied [5]. The permanent alignment hasn't received so much attention because it is generally very small, although large permanent alignment could be achieved by multi pulses [6].

Recently, a coherent emission around 391 nm is observed in the laser propagation direction when strong 800 nm femtosecond laser pulses propagate through nitrogen gas in the presence of an external seed containing 391 nm [7]. The coherent emission is identified as the transition of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and is attributed to seed-triggered superradiance [8,9]. However, the averaged superradiance signal decreased obviously when the polarization of the seed is changed from parallel to perpendicular relative to the pump laser polarization [10,11]. This phenomenon has been explained by the permanent alignment of N_2^+ ($B^2\Sigma_u^+$). However, the large permanent alignment cannot be explained by the general rotational excitation induced by strong femtosecond laser pulses.

Due to molecular orbital theory, nitrogen molecular ions in different electronic states can be considered to be generated through ionization from different molecular orbitals. Neutral nitrogen molecules have 14 electrons and its electronic configuration is $KK(\sigma_g2s)^2(\sigma_u2s)^2(\pi_u2p)^4(\sigma_g2p)^2$. The ionization from the highest occupied molecular orbital (HOMO) will leave N_2^+ in the ground electronic state (i.e. $X^2\Sigma_g^+$). In contrast, the ionization from HOMO-2 creates N_2^+ in the second excited electronic state (i.e. $B^2\Sigma_u^+$). Based on molecular Ammosov-Delone-Krainov (MO-ADK) theory [12], the ionization possibility is highly dependent on the angle θ between the molecular axis and the laser polarization direction in strong laser fields. In the case of N_2^+ ($B^2\Sigma_u^+$), it is generated through tunnelling ionization from HOMO-2 and the tunnelling ionization possibility decreases with increasing θ. The maximum ionization probability occurs at θ = 0° and the minimum at θ = 90° [13]. The anisotropic angle-dependant ionization results in the generation of aligned N_2^+ ($B^2\Sigma_u^+$), which may be the origin of the large permanent alignment of N_2^+ (B) observed in the experiment. But this speculation has not been proven.

The polarization of the fluorescence is always parallelled to the direction of dipole moment. The polarized fluorescence technique is often applied to measure dipole moment direction of large molecules [14] and widely used in the clinical and biomedical field [15]. Time-resolved fluorescence anisotropic technique further provides the rotation information of target under investigation and could be used to analyze dynamic behaviours of macromolecules, proteins and nanoparticles [16]. Because of fast rotation, fluorescence anisotropic technique is seldom used for small molecules in the gas phase. In this paper, we measured the fluoresce polarization of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) generated by strong femtosecond laser pulses. The fluorescence polarization exhibits an anisotropic angular distribution relative to the pump laser polarization. Through comparing the polarization properties of the fluorescence from ionized nitrogen molecules and neutral nitrogen molecules, we provide evidences that the large permanent alignment of N_2^+ ($B^2\Sigma_u^+$) origins from the preferential ionization of neutral nitrogen molecules by strong femtosecond laser pulses.

2. Experiment setup

Figure 1 illustrates the schematic diagram of the experimental setup. A Ti:sapphire laser amplifier system delivers linear-polarized femtosecond laser pulses with pulse energy of 3.6 mJ and pulse duration of 30 fs at repetition rate of 1 KHz. The laser pulses were focused by a lens with focal length of f = 30 cm into the gas chamber filled with pure nitrogen gas. The femtosecond laser pulses ionize nitrogen molecules and generate plasma filament. The fluorescence from the plasma filament was collected by a concave mirror and imaged outside the chamber. Then the image of the side fluorescence was introduced into a fiber connecting the

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spectrometer (AvaSpec-4096-SPU, Avantes Inc.) or the streak camera (C10910, Hamamatsu Inc.). Besides, a half-wave plate was inserted into the optical path to change the polarization direction of the pump laser. And a film polarizer (LPUV100, Thorlabs Inc.) with the spectral profile extending from 360 nm to 400 nm was placed before the detector to analyze the polarization of the fluorescence.

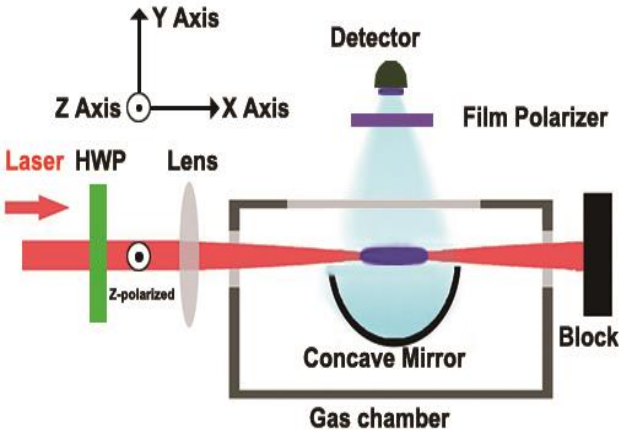

Figure 1: Experimental setup. Detector: fiber spectroscopy or streak camera.

3. Results and discussion

Figure 2 shows the polarized fluorescence spectra generated by linearly polarized pump laser pulses. The laser propagates along X axis with the polarization along Z axis. The fluorescence around the centre of the filament is collected in the side direction (Y axis). Black line represents the fluorescence emission with polarization along Z axis. While red line represents the fluorescence emission with polarization along X axis. Three strong emission lines locating around 375nm, 380nm and 391 nm were observed in the wavelength range between 360 nm to 400 nm. The emission lines around 375 nm and 380 nm respectively come from the transitions of N_2 ($C^3\Pi_u$, v'=1 → $B^3\Pi_g$, v=3) and N_2 ($C^3\Pi_u$, v'=0 → $B^3\Pi_g$, v=2), where v' and v are the vibrational quantum numbers of the upper and the lower electronic states. The emission line around 391 nm comes from the transition of N_2^+ ($B^2\Sigma_u^+$, v'=0 → $X^2\Sigma_g^+$, v=0). It is commonly accepted that N_2 ($C^3\Pi_u$) is generated by the collision between N_2 ($X^1\Sigma_g^+$) and free electrons in the laser plasma [17]. However, the formation mechanism of N_2^+ ($B^2\Sigma_u^+$) is still under debate [9,18,19]. There are two major channels in linearly polarized laser pulses. The first one is directly generated through tunneling ionization from HOMO-2. The second one is indirectly generated through tunnelling ionization from HOMO followed by the photoelectron recollision excitation. In this indirect channel, N_2^+ ($X^2\Sigma_g^+$) is firstly generated through tunneling ionization from HOMO and then is excited to the $B^2\Sigma_u^+$ state by the correlated electron collision. It can be seen that the fluorescence intensities emitted from N_2^+ ($B^2\Sigma_u^+$) and that from N_2 ($C^3\Pi_u$) show different polarization dependences. In the case of neutral nitrogen molecules, the fluorescence intensity is almost the same with the polarization along Z axis and X axis. However, the fluorescence from the ionized nitrogen molecular depends on the polarization. The fluorescence intensity polarized along Z axis is stronger by one third than that polarized along X axis.

In order to study the polarization properties of fluorescence in depth, we measured the fluorescence intensities at 391 nm and 380 nm as a function of polarization. The pump laser with polarization along Y axis is also included for comparison. Measured by rotating the film polarizer in XZ plane, the polarization distributions of the 391-nm and 380-nm fluorescence are shown in Figure 3. Red line represents the pump laser with polarization along Z axis and blue line represents the pump laser with polarization along Y axis. In Fig.3, the angle is recorded in the XZ plane and relative to Z axis. The angles 0° and 180° correspond to fluorescence polarization along Z axis, while angles 90° and 270° correspond to fluorescence polarization along X axis. The emission intensity at 380 nm is independent on the polarization whether the pump laser polarization is along Z axis or Y axis. Therefore, the fluorescence of excited neutral nitrogen molecules shows polarization independence, which is the common case for small molecules in the gas phase. The polarization independence also indicates that the permanent alignment caused by the rotational excitation is very small.

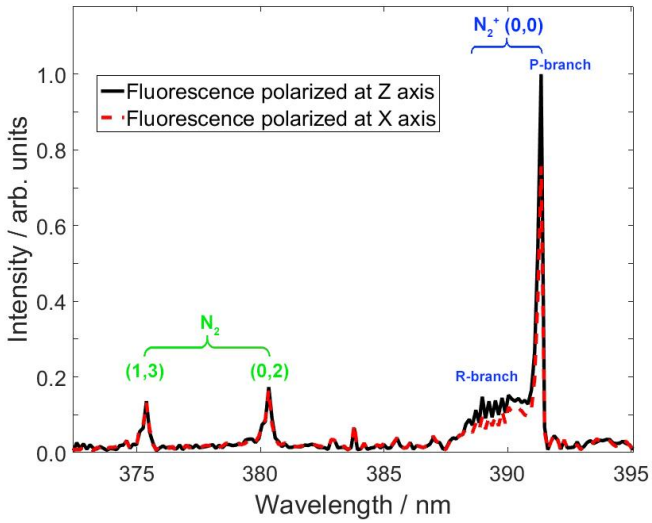

Figure 2: Fluorescence emission with polarization along Z axis (black line) and along X axis (red dashed line). The polarization of the pump laser is fixed along Z axis.

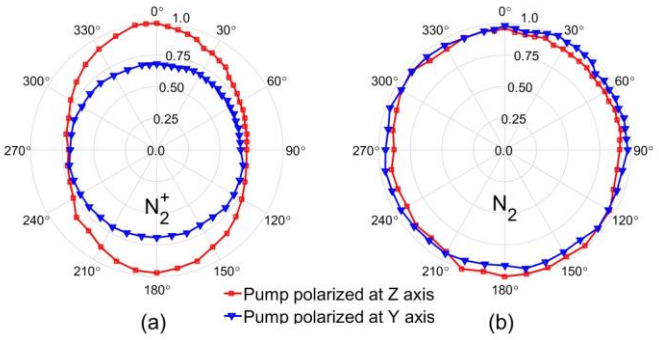

Figure 3: Fluorescence intensity at 391 nm (a) and 380 nm (b) as a function of the fluorescence polarization. Red line represents the pump laser polarization along Z axis and blue line along Y axis. The angle is recorded in the XZ plane and relative to Z axis.

In contrast, the emission intensity at 391 nm depends on the fluorescence polarization. When the pump laser polarization is along Y axis, the fluorescence intensity is isotropic in XZ plane. Because XZ plane is perpendicular to the pump laser polarization, it is expected that the distribution of fluorescence polarization is isotropic in XZ plane, which agrees with the observation. The agreement verifies the reliability of our measurement. However, when the pump laser polarization is along Z axis, the polarization-dependent fluorescence intensity becomes anisotropic in XZ plane. The fluorescence intensity with polarization along Z axis is stronger than that along X axis. In other words, the fluorescence intensity with polarization parallels to the pump laser polarization is stronger

than that perpendicular to the pump laser polarization. It should be emphasized that the dipole moment between N_2^+ ($B^2\Sigma_u^+$) → N_2^+ ($X^2\Sigma_g^+$) is parallel to the molecular axis [18,19]. The stronger fluorescence intensity with polarization parallel to the pump laser polarization means that the yield of N_2^+ ($B^2\Sigma_u^+$) is higher with molecular axis along the pump laser polarization. This phenomena is consistent with the angular-dependent ionization probability of nitrogen molecules in strong femtosecond laser fields. The maximum ionization probability for HOMO-2 occurs when the molecular axis is parallelled to the laser polarization [13]. As a result, the molecular axis of the generated N_2^+ ($B^2\Sigma_u^+$) is preferentially distributed in the pump laser polarization direction.

The fluorescence recorded in Fig. 2 and Fig. 3 is an integral signal. The anisotropic distribution of fluorescence polarization represents the average alignment degree of N_2^+ ($B^2\Sigma_u^+$) over the total integral time. Because the polarization of the 391-nm fluorescence is parallelled to the molecular axis of N_2^+ ($B^2\Sigma_u^+$), the alignment degree can be calculated through the measured anisotropic distribution of fluorescence polarization. When the pump laser polarization is along Z axis, the fluorescence intensity with polarization along Z axis is proportional to $\langle\cos^2\theta\rangle$, where θ represents the angle between the molecular axis of N_2^+ ($B^2\Sigma_u^+$) and the laser polarization direction. Instead, the fluorescence intensity with polarization along X axis is proportional to $\langle\sin^2\theta\rangle/2$. Due to the data in Fig.2 and Fig. 3, the intensity ratio is about 4:3 for the fluorescence with polarization parallel to the pump laser polarization to that perpendicular to the pump laser polarization. Namely, the ratio of $\langle\cos^2\theta\rangle$ to $\langle\sin^2\theta\rangle/2$ is 4:3. As a result, $\langle\cos^2\theta\rangle$ is determined to be 2/5. If the angular distribution of molecular axis is isotropic relative to the laser polarization, $\langle\cos^2\theta\rangle$ equals 1/3. The value of 2/5, higher than 1/3, demonstrates the degree of the permanent alignment of N_2^+ ($B^2\Sigma_u^+$) generated by strong-field angular-dependent ionization.

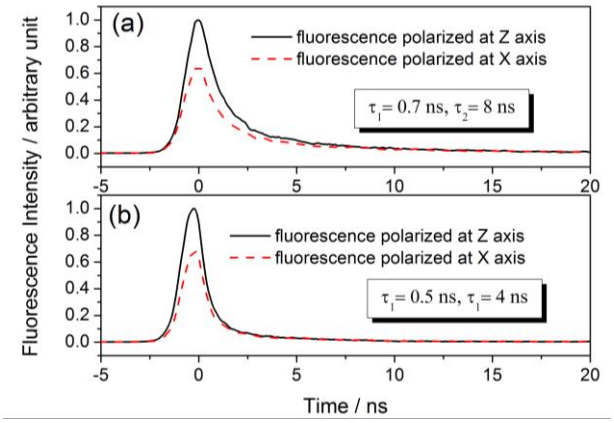

Figure 4: Temporal profile of fluorescence intensity at 391 nm at the pressure of 1 mbar (a) and 4 mbar (b). Black line represents the fluorescence emission with polarization along z axis and red dashed line represents the fluorescence emission with polarization along x axis. The pump laser polarization is fixed and along z axis.

However, the population evolution is very complicated for excited nitrogen molecules in plasma filamentation. In addition to the spontaneous emission observed in Fig. 2, the excited nitrogen molecules will be quenched by collision. Here, we recorded the time-resolved fluorescence emission using a picosecond streak camera. Figure 4 show the temporal profile of fluorescence intensity at 391 nm generated by strong 800 nm laser pulses with polarization along Z axis. The fluorescence decay contains two components. The slow exponential component is in the nanosecond range, corresponding to the decay of N_2^+ ($B^2\Sigma_u^+$) by the collision of nitrogen molecules as well as the spontaneous emission [20]. The fast component is in the sub-nanosecond range, corresponding to the decay of N_2^+ ($B^2\Sigma_u^+$) by the collision of free electrons in the plasma filamentation [21]. When the gas pressure is increased, the densities of collision partners are increased as well. Here the collision partners are neutral nitrogen molecules and free electrons. As a result, the collision time becomes shorter and fluorescence decay becomes faster for both the slow component and the fast component. Fig. 4(a) and Fig. 4(b) show the time-resolved fluorescence emission recorded at the gas pressures of 1 mbar and 4 mbar, respectively. Indeed, the fluorescence decay becomes faster for both the slow component and the fast component with increasing gas pressure.

In Fig. 4, black line represents the fluorescence emission with polarization along Z axis and red dashed line represents the fluorescence emission with polarization along X axis. It can be seen that the intensity ratio for the fluorescence with polarization parallel to the pump laser polarization to that perpendicular to the pump laser polarization is time dependent. The maximum ratio is about 1.5. The ratio has not obviously changed during the period corresponding to the fast decay component of fluorescence. Instead, the ratio is decreased and approaches unity with time during the period corresponding to the slow decay component of fluorescence. As we have discussed, the fast decay component of fluorescence is caused by the collision of free electrons and the slow one by the collision of molecules. This observation indicates that the free electron collision will not destroy the permanent alignment of N_2^+ ($B^2\Sigma_u^+$). However, the permanent alignment will be destroyed by the collision of molecules. Based on the ratio of 1.5 for the fluorescence with polarization parallel to the pump laser polarization to that perpendicular to the pump laser polarization, $\langle\cos^2\theta\rangle$ is calculated to be 3/7, which represents the nascent permanent alignment degree.

Field-free permanent alignment can be understood by different behaviors of M and J in strong laser fields, where J is the quantum number of rotational angular momentum, and M the projection of J on the laser polarization direction (here is Z axis). For the rotational states with M = 0, the rotational axis is perpendicular to Z axis, so the molecular axis is always in the plane containing Z axis. As a result, $\langle\cos2\theta\rangle$ equals 1/2. For the rotational states with M = J, the rotational axis is along z axis, so the molecular axis is always in the plane perpendicular to Z axis. As a result, $\langle\cos2\theta\rangle$ equals zero. For field-free molecular alignment, permanent alignment exists if $\langle\cos2\theta\rangle$ is time-independent and the value is different from 1/3, although the permanent alignment is not large under normal condition. Under current experimental condition, N2+ (B2Σu+) is generated through tunneling ionization from HOMO-2. It is also generated through tunneling ionization from HOMO followed by photoelectron recollision excitation. According to MO-ADK theory, the ionization possibility is maximum when the molecular axis is parallel to the pump laser polarization for both HOMO-2 and HOMO [13]. As a result, the molecular axis of most initially generated N2+ (B2Σu+) is along Z axis, which means that M is close to 0, and a permanent alignment is therefore generated. In comparison with the small permanent alignment of neutral molecules generated by the laser-driven molecular rotational excitation, the permanent alignment can be large for nitrogen molecular ions generated by strong-field ionization. The large permanent alignment of N2+ (B2Σu+) agrees with previous experimental observations on superradiance triggered by external seed with parallel and perpendicular polarization [10,11].

4. Conclusions

Strong femtosecond laser pulses propagate in nitrogen gas, the ionized nitrogen molecules in excited electronic states will decay to the ground electronic state through fluorescence emission. We measured the polarization distribution of the fluorescence at 391 nm corresponding to the transition of N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$). The intensity ratio is determined to be 1.5 for the fluorescence with polarization parallel to the pump laser polarization to that perpendicular to the pump laser polarization. Because the dipole moment between N_2^+ ($B^2\Sigma_u^+$) → N_2^+ ($X^2\Sigma_g^+$) is parallel to the molecular axis, the fluorescence polarization is always parallel to the molecular axis. The preferential distribution of fluorescence polarization along the laser polarization indicates a permanent alignment exists for N_2^+ ($B^2\Sigma_u^+$), which is characterized by $\langle\cos^2\theta\rangle$ = 3/7. The large permanent alignment is attributed to the angular-dependent ionization probability of nitrogen molecules by strong femtosecond laser pulses. Whether N_2^+ ($B^2\Sigma_u^+$) is generated through tunnelling ionization from HOMO-2 or HOMO followed by photoelectron recollision excitation, its axis is mainly distributed along the laser polarization direction. As a result, the permanent alignment is generated, which can survive sub-nanosecond depending on the gas pressure. The large permanent alignment of N_2^+ ($B^2\Sigma_u^+$) well explains previous experimental observations on superradiance triggered by external seed with polarization parallel and perpendicular to the pump laser polarization.

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