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Molecular alignment using circularly polarized laser pulses

C T L Smeenk1 and P B Corkum

JASLab, University of Ottawa and National Research Council, 100 Sussex Drive, Ottawa, Canada
E-mail: christopher.smeenk@mbi-berlin.de

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Abstract

We show that circularly polarized femtosecond laser pulses produce field-free alignment in linear and planar molecules. We study the rotational wavepacket evolution of O₂ and benzene created by circularly polarized light. For benzene, we align the molecular plane to the plane of polarization. For O₂, we demonstrate that circular polarization yields a net alignment along the laser propagation axis at certain phases of the evolution. Circular polarization gives us the ability to control alignment of linear molecules outside the plane of polarization, providing new capabilities for molecular imaging.

(Some figures may appear in colour only in the online journal)

Control of molecular alignment and orientation is an essential element of many contemporary experiments in molecular imaging and reaction dynamics [1]. There are two general approaches to alignment—adiabatic and non-adiabatic. State of the art techniques use supersonic molecular beams and a state selector to direct molecules of a single ro-vibrational state into an ultra-high vacuum chamber [2, 3]. By applying a strong non-resonant laser pulse, either adiabatically or non-adiabatically, the most polarizable axis of the molecule can be aligned in the laser field direction of linearly polarized light [1]. Incorporating an elliptically polarized nanosecond pulse allows planar alignment of the major and minor polarizability axes in asymmetric top molecules [4–6]. Both linear and elliptically polarized aligning pulses control molecular rotation.

For many applications it is important to study molecules aligned outside the plane of polarization. For example, we could record molecular frame photo-electron angular distributions (MF-PADs) of k-aligned linear molecules from a new direction with circularly polarized probe pulses [7]. This kind of experiment is not possible when molecules are aligned in the polarization plane. We show how k-alignment can be achieved. Thereby, we open a third co-ordinate over which we can control the molecular frame-of-reference.

The concept of our experiment is sketched in figure 1. We create a rotational wavepacket in O₂ using a moderately intense circularly polarized aligning pulse. To determine the dynamics of the wavepacket, including its k-alignment, we use a second high intensity circularly polarized pulse to Coulomb explode the molecule. In a circularly polarized aligning pulse, the most polarizable axis of the molecule receives a torque into the plane of polarization (xy—see figure 1). This creates a rotational wavepacket that re-aligns to the plane of polarization every full revival period $T_R$. For a linear molecule, just before the full revival the internuclear axis first aligns along the direction of laser propagation, z (figure 1; inset left). We call this ‘k-alignment’. The molecules continue to rotate and a short time later the internuclear axis is aligned with the plane of polarization (figure 1; inset right). Thus circularly polarized aligning pulses allow us to control molecular alignment outside the plane of polarization, along the laser k-axis. This completely optical method applies to any molecule that possesses anisotropic polarizability in a single direction.

We also demonstrate the utility of non-adiabatic alignment with circular polarization by using it to control benzene, a symmetric top. In benzene it is useful to concentrate on

1 Present address: Max Born Institute for Nonlinear Optics, Max-Born-Straße 2A, D-12489 Berlin, Germany.
the vector normal to the plane containing the carbon and hydrogen nuclei. Planar alignment of benzene corresponds to aligning the normal vector along the $k$-axis (figure 1 left). Anti-alignment of benzene corresponds to the normal vector de-localized in the plane of polarization (inset left). For a slightly longer pump-probe delay the molecular alignment is confined to the plane of polarization (inset right). A circularly polarized probe pulse shown in red explodes the molecules to determine the direction of alignment.

Experimentally, we use circularly polarized 60 (250) fs pulses produced in a Ti:sapphire laser system operating at 800 nm to align $O_2$ ($C_6H_6$). The pump laser intensity was $4 \times 10^{13}$ W cm$^{-2}$ ($2 \times 10^{13}$ W cm$^{-2}$). The pump pulse is focused by an $f$/25 parabolic mirror onto a pulsed, supersonic gas jet (Even–Lavie valve) operating at 500 Hz. To measure $O_2$ alignment we use neat gas at 8.5 bar backing the valve. The jet temperature is estimated to be 5 K. For benzene alignment we use a gas mixture of 10 mbar benzene in 100 bar He. The pressure of the mixture backing the pulsed valve was 14 bar.

We use a circularly polarized probe pulse to explode the molecules and measure the fragment momentum vector in a velocity map imaging spectrometer (VMI). The VMI records a differential two-dimensional projection of the fragment momentum distribution, $d^3N/dp_x dp_y dp_z$. The probe is focused onto the sample of aligned molecules with the same parabolic mirror at $f$/12.5. The pump-probe delay is precisely controlled by an automated delay stage. By measuring the momentum distributions from exploded $O_2^+$ fragments, we measure a degree of alignment of $(\cos^2 \theta) = 0.7$ using a linearly polarized pump pulse. To determine the molecular alignment angle $\theta$ using a circularly polarized pump pulse, we measure the fragment momentum with respect to the $z$-axis, $\cos \theta = p_z/p$. The degree of alignment in the wavepacket is then given by the fragment momentum distribution projected onto the $z$-axis,

$$
\langle \cos^2 \theta \rangle = \int_0^\pi d\theta \cos^2 \theta \left( \int \frac{d^3N}{dp_x dp_y dp_z} dp_z \right)
$$

$$
= \int_{-p}^{+p} dp_z \frac{p_z^2}{p^2} \left( \int \frac{d^3N}{dp_x dp_y dp_z} dp_z \right).
$$

Since the VMI records a 2D projection of the momentum distribution, we do not know the full 3D momentum of each fragment. We estimate $p$ by measuring a momentum distribution of fragments from Coulomb explosion of randomly aligned molecules. This approach likely underestimates the degree of alignment in the rotational wavepacket.

Measuring the fragment momentum with respect to the $z$-axis inverts the typical revival shape compared to measuring $\theta$ with respect to the polarization axis [1, 8]. In a circularly polarized aligning pulse the molecules are initially pulled into the plane of polarization, $\theta = \pi/2$. Hence planar alignment corresponds to a minimum in the $(\cos^2 \theta)$ alignment parameter, sketched as the green curve in figure 1. Anti-alignment or $k$-alignment yields fragments aligned parallel to the $z$-axis: $\theta = \{0, \pi\}$. Therefore $k$-alignment corresponds to a maximum in the alignment parameter. This is the opposite of the behaviour one observes when measuring the alignment angle with respect to the polarization axis [1, 8].

In our experiment the explosion pulse is 50 fs long (FWHM). At this duration detecting alignment using Coulomb explosion by an intense infrared pulse introduces a bias into the measurement. The $O_2^+$ fragments used to determine the molecule’s alignment in the lab frame are produced mainly by enhanced ionization [9–11]. Enhanced ionization selects those molecules lying in the plane of polarization. Hence the portion of the rotational wavepacket lying outside the plane of polarization is much less likely to produce the highly charged fragments we use to measure alignment. Using Coulomb explosion by an infrared circularly polarized laser pulse therefore means our probing technique is less sensitive to molecules aligned outside the plane of polarization. We will show that we are still able to make a relative measurement of planar and $k$-alignment using Coulomb explosion. However, the bias introduced by enhanced ionization prevents us from quantitatively determining the degree of alignment. This could be partially improved on by using a few cycle explosion pulse [12].

The rotational wavepacket evolution of $O_2$ created by a circularly polarized pump pulse is shown in figure 2(a) as seen through the $O_2^+$ fragments. Initially the molecules are pulled into the plane of polarization, $xy$. Since the angle $\theta$ is measured with respect to the $z$-axis, the alignment parameter $(\cos^2 \theta)$ initially decreases relative to the value for unaligned molecules $\approx 0.24$. The decrease in $(\cos^2 \theta)$ during the first 250 fs corresponds to planar alignment of $O_2$. Subsequently, the wavepacket evolution has a similar temporal behaviour as the rotational wavepacket excited in $O_2$ by a linearly polarized pulse [8]. The quarter revival (2.90 ps) exhibits strong planar alignment, while at the three-quarter revival (8.68 ps) molecules are preferentially aligned along the $k$-axis. The strong quarter and three-quarter revivals in $O_2$ are well known and appear because oxygen has nuclear spin $I = 0$ and therefore only odd rotational states are populated in $O_2$ [8]. The full revival occurs at $T_R = 11.70$ ps just as with a linearly polarized pump pulse. At the full revival $k$-alignment is immediately followed by planar alignment. This behaviour is the inverse of the half revival (5.85 ps) where planar alignment

![Figure 1](image-url) Just prior to the full revival in circularly polarized light (sketched in green), the molecular alignment distribution (inset, blue) is parallel to the propagation axis, $z$. This is ‘$k$-alignment’ (inset left). For a slightly longer pump-probe delay the molecular alignment is confined to the plane of polarization (inset right). Anti-alignment of benzene corresponds to the normal vector de-localized in the plane of polarization (figure 1 right).
Figure 2. Rotational wavepacket dynamics of O₂ using a circularly polarized pump pulse. (a) The wavepacket revival shows strong 1/4, 1/2, 3/4 and full revivals. The full revival period \( T_R = 11.7 \) ps. (b) \( \text{O}^+ \) fragment momentum distribution at planar alignment \( (T_R/4 = 2.90 \) ps\). (c) \( \text{O}^+ \) fragment momentum distribution at \( k \)-alignment \( (3T_R/4 = 8.68 \) ps\). (d) Integrated \( \text{O}^+ \) distributions along the propagation axis at planar and \( k \)-alignment.

precedes \( k \)-alignment. Each of these temporal features was seen before in alignment using linearly polarized light [8]. By using a circularly polarized aligning pulse we have observed alignment in a new direction: along the laser \( k \)-axis.

The \( \text{O}^+ \) momentum distributions provide direct evidence of planar alignment and \( k \)-alignment (figures 2(b) and (c)). The fragment momentum spectra are dominated by enhanced ionization and therefore the maximum signal is always in the plane of polarization. However, the \( \text{O}^+ \) distribution at the 3/4 revival (figure 2(c)) is extended along the \( z \)-axis. This is the signature of net \( k \)-alignment. Conversely the fragment distribution at 1/4 revival (figure 2(b)) is more narrowly confined to the plane of polarization. This is due to planar alignment at the quarter revival. The contrast between planar and \( k \)-alignment is more clear when comparing the projection of the respective distributions onto the \( k \)-axis (figure 2(d)). It is clear the distribution at \( k \)-alignment is significantly more extended along the \( z \)-axis.

Our circularly polarized pump pulse produces a torque on linear molecules because of a polarizability asymmetry along one of the principal axes. This pulls the molecular axis into the plane of polarization. A similar polarization asymmetry occurs in symmetric and asymmetric top molecules, and was exploited to create 3D alignment of asymmetric top molecules using nanosecond pulses [4–6]. In benzene, a symmetric top, the polarizability along the two principal axes in the molecular plane is larger than along the axis normal to the molecular plane [13, 14]. This asymmetry means the dipole induced by a strong non-resonant laser pulse will be larger in the molecular plane than along the normal axis. This leads to a net torque on the molecule by our 250 fs pump pulse, and field-free alignment of the molecular plane with the plane of polarization. At planar alignment the normal vector lies parallel to the \( k \)-axis. As the molecule continues to rotate the molecule aligns. At anti-alignment the normal vector lies in the plane of polarization.

During the Coulomb explosion of benzene, H⁺ fragments are produced with a broad angular distribution but maximum emission probability in the molecular plane [6, 15]. We use the direction of H⁺ emission as a surrogate for the direction of the molecular plane. By recording the H⁺ momentum distribution as a function of pump-probe delay, we can watch the rotational wavepacket evolution (figure 3(a)). In figure 3(a) the circularly polarized pump pulse initially pulls the molecules into the plane of polarization, leading to a decrease in \( \langle \cos^2 \theta \rangle \) at prompt alignment. At 44.1 ps the half revival occurs with anti-alignment maximizing at 44.4 ps. In figure 3(a) the full revival occurs at 88.0 ps. We do not observe quarter revivals in benzene. At anti-alignment, the exploded protons are emitted in a broad angular distribution from anti-aligned molecules (figure 3(b))². This is in contrast to the proton distribution from planar molecules at 88.4 ps where the protons are confined more narrowly to the plane of polarization (figure 3(c)). The contrast between planar alignment and anti-alignment is more clear when viewing the proton distributions projected onto the \( k \)-axis (figure 3(d)). We observe a substantially narrower proton distribution at 88.4 ps from Coulomb explosion of molecules aligned in the plane of polarization. Thus, circularly polarized light allows us to create field-free alignment of a planar molecule.

In conclusion, we have shown how to gain added control over non-adiabatically aligned molecules. Controlling molecular alignment with circular polarization allows us to achieve two goals: (1) we can create field-free alignment

² In figures 3(b) and (c) there is a small detector imperfection that reduces signal in the upper left-hand corner, however, this does not strongly affect the measurement since it is at the edge of the distribution.
of planar molecules in the plane of polarization, (2) we can create a net alignment of linear molecules outside the plane of polarization (i.e. k-alignment). This allows molecular structure to be studied from a new direction. Although we used Coulomb explosion to observe the alignment, our all-optical technique is not limited to any specific probing method. It can easily be used with higher density gas sources such as those needed for HHG, XUV transient absorption, or ultrafast x-ray diffraction [16–18]. All methods for studying ultrafast structure and dynamics will benefit from the additional control over the molecular frame of reference that we have demonstrated.

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