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Selective manipulations of molecular rotations

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Abstract

In the last years, the interest in molecular alignment and orientation has been constantly increasing. The reason lies in the variety of applications in chemistry, physics, nano-sciences and nonlinear optics based on molecular alignment. The main developments presented in this thesis deal with manipulations of molecular rotations with ultrashort laser pulses. We focus on control schemes for selective rotational excitation of molecular species having close chemical and physical properties. The presented control schemes are based on the interaction of the molecular ensembles with two laser pulses. The first pulse always interacts with molecules having isotropic molecular angular distribution. This interaction is followed by dynamic molecular evolution under field free conditions. The effect of the second pulse applied to the molecular ensemble at specific delay depends on the molecular situation at the time of interaction. In our work, we discuss the molecular angular evolution both classically and quantum mechanically starting from basic principles. By controlling the time delay between the two pulses we selectively affect the rotational motion of molecular isotopes (isotopologues), and nuclear spin modifications (para and ortho). Additional control of the pulses’ relative polarization axes is shown to result in induced unidirectional molecular rotation. The control of the sense of rotation (clockwise / counterclockwise) is accompanied with highly anisotropic angular distribution, offering an efficient way for controlling chemical kinetics as well as the optical properties of the medium. All of the control schemes presented here are based on nonlinear, non resonant interactions and therefore are not molecule-specific and general for all linear molecules.
מבוא

האחרונות לשנים,..., מולקולות שלוכיווןיישורבנושא המדעי בעניין מתמדת, עליה ישנה. הנעוצת הסיבות הכימיה בתחומי השימושים בولوجي, הפיסיקה - ליניארי והאופטיקה, נתנו הפיזור על המבוססים מולקולות של הזווית שלسلوكיה. ההסבתה, באמצעות שלפניכם הדוקטורט,摆在מעון של שלחית ב컷ות שלפניכות. ב),$ פיזור בעלות מולקולות צבר על אייזוטרופי כוווני, אלקטרומגנטי השדה של השפעה ללא מולקולארי סיבוב שלדינמיקהтанילה בעקבותיו. היאстра פולס שני עם מולקולות שליטה השתקת שלפניכות יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יאיר, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, הפולסים שני שבין חום שליטה יアイ, נמצאת ת.HandlerFunc של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפיזור של הפקעט.
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1.1 Introduction

Originally, spectroscopy was the study of the interaction between radiation and matter as a function of wavelength. In fact, historically, spectroscopy referred to the use of visible light dispersed according to its wavelength, e.g. by a prism. Later the concept was expanded greatly to comprise any measurement of a quantity as function of either wavelength or frequency. Generally, in all of the spectroscopic techniques, light is shined onto a molecular sample (gas, liquid or solid phase) and collected by a detector to reveal changes in the properties of the original light. In the numerous spectroscopic techniques currently available, various kinds of detectors are used (wavelength sensitivity, intensity etc.), depending on the light-property of interest. These changes in the property of light reflect fundamental molecular properties such as electronic energy levels, molecular degrees of freedom (vibrations and rotations), nuclear properties etc.

The aim of most conventional methods is to gain knowledge on the substrate under investigation therefore the properties of the light applied to the sample should be manipulated by the interaction with the molecular target, but the target has to remain unchanged during the interaction. To overcome this contradiction, the light intensities used in conventional spectroscopy are kept as low as possible in order to interfere and alter the molecular electronic properties as little as possible. This region of light intensities is the perturbative region in which the molecular sample gains or loses energy due to the interaction with the electromagnetic field, however, it’s electronic structure, vibrational frequencies or any other molecular property remain unchanged, and the spectroscopic signal, reflects the molecular properties as close as possible to the field-free molecular case. A complementary approach to frequency domain spectroscopy is performed in the time domain. In time domain spectroscopy, the relative time delays between the pulses are controlled and the molecular evolution is probed. Fourier transformation switches between the time and frequency domain, thus the data collected in both domains provides the same information. An hybrid approach of combined time and frequency measurements have shown to provide additional information and better understanding of molecular evolution in several cases [1,2,3,4].

With the development of intense lasers and the availability of intense light sources, new research fields have emerged, in which molecular samples are being manipulated by strong electromagnetic fields. Physically, a molecule subjected to strong electromagnetic radiation is modulated by the field and should be considered as such in order to correctly predict the results of such interaction. The Stark effect [5], describing the splitting in spectral lines by electromagnetic fields may be the most basic phenomenon of this region. The region of light intensities exceeding the perturbative limit was and is vastly explored; non linear spectroscopic methods[6,7] starting from two photon

The use of lasers as sources of coherent electromagnetic radiation, intense enough to affect matter (may it be atomic/molecular/crystal in the gas/liquid or solid state) gave birth to the field of Coherent Control. **Coherent control** is a quantum mechanical based method for controlling dynamical processes with light, employing quantum interference phenomena which are controlled by the phases of laser pulses [12,13,14,15].

In principle, two coherent laser sources of different frequencies can be used for controlling population transfer in simple molecules. A well known scheme applied to the simplest three level systems for controlling population transfer between states known as Stimulated Raman Adiabatic Passage (STIRAP) was demonstrated, where population cycling between two pairs of coupled energy levels can lead to complete population transfer to a prechosen level. In the most basic STIRAP [16] scheme, two laser frequencies were used. However, the constant development of short laser pulses, has led to the development much richer control schemes. Ultrashort laser sources commercially available nowadays, offer pulses as short as a few femtoseconds. The uncertainty principle connecting the time and frequency domains, suggests that such short pulses have very broad frequency band according to $\Delta \omega \times \Delta \tau \geq \hbar$. Typically, a laser pulse of 50fs centered around 800nm, has a gaussian spectral shape with FWHM around 35nm, comprised of $\sim 10^5$ phase-locked cycles coming from the laser oscillator. In the various control schemes, the phases of these frequencies are manipulated (shaped) in order to drive the molecular sample to a desired goal. A lot of work has and is being done in the field of pulse shaping for controlling processes taking place in molecular samples. The designing of pulse shapes [17] requires prior knowledge of the molecular energy levels spread over the electronic, vibrational and rotational degrees of freedom and complete control of molecular dynamics or populations is yet to be achieved, although many control schemes have been demonstrated to successfully affect specific molecular systems and drive them to well defined goals. Optimal[18] and local[19] control schemes are two examples of pulse-shape design protocols. In the late 1990’s, the focus of the field has moved to iterative shaping using genetic algorithms [20,21]. In this method, the computer controls the shape of the pulses applied in the experiment by applying voltages to the different pixels of a Spatial Light Modulator (SLM) through which the dispersed pulse propagates. The observable in interest is fed to the computer as well. At the first stage, the computer chooses ten arbitrary pulse shapes serving as the first generation, applies them to the system and collects the readings of the observable target. In principle, each pulse shape is a vector of voltages which are applied to the SLM pixels. At the next step, the computer generates
the next generation by mixing parts of the vectors (genes) from the previous generation. The statistical weight of the previous generation depends on the measurement of the target observable. That way, the chance of compatible vectors ('good genes') to survive in the next generation is better than the chance of 'bad genes'. This iterative process takes place several times until a good voltage vector (corresponding to a pulse shape) is reached and cannot be improved. Although this method has been proven to work in many cases, genetic algorithms offer better results, but not always the best due to the existence of local maxima in the complex optical phase map and the iterative nature of the described phase shaping process. Nowadays, the interest in genetic algorithms has declined somewhat, mainly since the physics and chemistry incorporated in the laser-matter interaction is not reflected and is almost impossible to extract. One scheme for extracting the interesting physical molecular properties was suggested, where a mathematical process known as Principle Component Analysis (PCA)[22] was used, however this scheme has not been significantly explored and demonstrated yet. Basic pulse shapes such as the positive/negative chirp[23], sinusoidal phase[24] and pi phase steps[25] are being used extensively[26]. In section 6.2 the effect of chirped pulses will be discussed in the context of molecular alignment.
1.2 Previous work in the field of molecular alignment

In the quest for better control of molecular angular distribution, a number of methods have been used to orient molecules via interaction with static or time-dependent electromagnetic fields[27].

Renewed interest in these problems was triggered by experiments demonstrating that short intense laser pulses tend to align the molecular axis along the direction of the field polarization (for early experiments see refs.[28,29,30,31]). When a laser pulse acts on a molecule, it induces an electric dipole in the molecule, which in turn interacts with the laser electric field. As molecular polarizability is generally anisotropic, such an interaction leads to the alignment of the molecule along the direction of the laser pulse polarization. A strong enough laser field creates pendular molecular states [32,33,34] that are hybrids of field-free rotor eigenstates. By adiabatically turning the laser field on, it is possible to trap a molecule in the ground pendular state, thus leading to molecular alignment. Early studies on laser-induced molecular alignment were performed with pulses of nanosecond duration, long compared to typical molecular rotational times. Under these conditions, a rather modest alignment may be achieved during the pulse, and the alignment vanishes after the pulse. Behavior of molecules in a general, strong, time-varying field is a much less-studied problem, although it was well understood that nonadiabatic excitation by short laser pulses induces long-persisting beats in the molecular angular distribution[35,36,37,38,39].

Since mid 1990s, several groups (including ours) realized that ultra-short (100 fs and less) pulse excitation of molecular rotational wave packets may result in a considerable transient molecular alignment after the laser pulse is over, i.e. at field-free conditions [40,41,42,43,44,45,46]. A certain degree of field-free alignment was observed both for small diatomic molecules as well as for more complex molecules such as iodobenzene [47]. If a molecule is subject to an electric field, it tends to be aligned parallel to the applied field direction. Once created, aligned state will periodically regenerate because of the effect of quantum revivals [40,44,48,49,50]. This phenomenon paves the way for many applications that require only a transient molecular alignment, where the molecular angular distribution briefly becomes narrow at some predetermined time. A number of such applications are presented in the recent review [51], including the use of field-free aligned molecules for quantum information processing [52,53] and it’s first experimental demonstration [54], pulse compression [55], and phase modulation by rotational wavepacket revivals[56,57]. In the last few years, pre-alignment of molecules is used for generation of high harmonics for molecular holography [58,59]. Molecular alignment has been shown to play a significant role in filamentation of strong ultrashort laser pulses [60, 61, 62]. New x-ray laser sources such as the free electron x-ray laser at SLAC are predicted to yield x-ray diffraction images from femtosecond x-ray laser pulses, a
process that requires high degree of molecular alignment at the moment of interaction, and the list of applications is constantly growing.

The quality of the alignment of a linear molecule is usually described by the maximal value of $<\cos^2(\theta)>$ that is achieved by an ensemble of laser-excited molecules. Here $\theta$ is the angle between the molecular axis and the direction of the laser electric field, and the angular brackets mean averaging over the initial molecular ensemble. Previous studies have mostly considered rotational control by a single laser pulse. It was shown that there is a limit to the degree of molecular alignment that can be attained by a single, ultrashort laser pulse [63]. It is clear that in order to achieve higher degree of alignment, stronger laser pulses should be used. However, upon interaction with high intensity fields, processes such as multiphoton ionization and dissociation start taking place, therefore there is a practical limit to the power to be used. In order to overcome this problem, a more intuitive approach to enhanced molecular alignment/orientation based on multiple laser pulses[45,63,64,65,66] was suggested, and was later demonstrated[67,68,69] to yield high degrees of transient molecular alignment.

Several techniques have been applied for the detection of molecular alignment. Following a strong aligning pulse, a linearly polarized probe pulse is applied. Weak field polarization technique relies on the change of polarization due to the birefringence experienced by the probe due to its interaction with an aligned ensemble [70, section 3.3]. Another method for the mapping of the molecular angular distribution after the (first) aligning pulse is by applying an energetic (second) pulse which causes a dissociative ionization of molecules to fragments which are accelerated by a strong electrostatic field (Coulomb explosion). The kinetic energy and spatial distribution are detected and the angular distribution of the molecules prior to dissociation is determined [71,72,73]. Another method (which we use and which will be explained in details) relies on the third order non-linear response of the medium. This method was first applied by Dantus et.al.[74], who studied the quantum rotational, and vibrational wavepacket revivals, and explored the saturation effects on the rotational dynamics [75]. Alignment of more complex molecules such as Iodobenzene and methyl iodide was shown to be feasible [76], and selective photodissociation of linear molecules such as N$_2$[77], I$_2$[78] and CO[79] was demonstrated. Several groups have achieved, higher degree of control over rotational wavepackets via pulse shaping [80,81], but still most experiments in this field, rely on multiple laser pulses applied at controlled delay times.
2. Theoretical background

2.1 Classical description

When molecules with a permanent dipole moment (such as HCl, KI etc) are subject to a DC electric field, they orient parallel to the direction of the applied field. The torque exerted on a molecule is proportional to the projection of the field perpendicular to the molecular dipole moment axis \( \tau \propto -\sin(\theta) \) (where \( \theta \) is the angle between the molecular axis and the electric field). In molecules lacking permanent dipole moment, a similar effect can be achieved if the molecule is anisotropically polarizable. In this case, a strong enough electric field induces an electric dipole and interacts with the dipole. The induced dipole in the direction of the molecular axis is proportional to \( \mu_{\text{induced}} = \Delta \alpha \Delta E \cos(\theta) \), and the interaction energy is given by \( V = \Delta \alpha E^2 \cos^2(\theta) \). Thus, the torque exerted on the molecule is given by \( \tau \propto dV/d\theta \propto -\sin(2\theta) \). In principle, this claim is also valid for molecules having permanent dipole moment, as long as they present polarizability anisotropy. For the sake of simplicity, let us consider the effect of such interaction on an ensemble of molecules at zero temperature (no angular velocity), distributed isotropically in a plane. The torque exerted on a molecule initially aligned at an angle \( \theta \) to the field polarization is proportional to \(-\sin(2\theta)\). A typical rotational time for a small molecule is of the order of several picoseconds. Thus, with pulses of picoseconds (or longer) duration, reorientation and alignment occurs during the pulse. However, with femtosecond pulse duration a molecule can be regarded as frozen during the pulse. When a torque is applied, the molecule gains angular velocity but significant reorientation will only take place after the pulse is over, i.e. reorientation occurs under field-free conditions. Thus, the angular velocity that a molecule gains is proportional to the torque exerted by the field, as is shown in figure 1a. Propagation forward in time according to their induced angular velocities will result in squeezed angular distribution, peaking in the direction of the applied field polarization (Figure 1b).
Figure 1: (a) Isotropically distributed molecules subjected to an ultrashort laser pulse polarized along the z axis. Angular velocities are depicted by the black arrows. (b) Rotation according to their acquired angular velocities results in the non isotropic angular distribution (‘alignment’).

The typical time for a small molecule to align is around few hundreds of femtoseconds (depending on the pulse strength and on the molecular properties). Classically, in the absence of additional fields, the molecules will continue to rotate and will never reach alignment or any other squeezed angular distribution again. However, molecules are quantized entities and should be treated as such, and in our case, the most pronounced manifestation the rotational energy quantization is the well know phenomenon of quantum revivals [82, 83].

2.2 Quantum revivals
Quantum-mechanically, a laser pulse excites a wave packet which is formed from many rotational states, and which may be written as:

\[ |\psi(\theta,t)\rangle = \sum_{J,m} c_{J,m} |J,m\rangle \exp(-i E_J t) \]  

(1)

Where \(|J,m\rangle\) represent the eigenstates of the rotor (spherical harmonics). For linear molecules (treated as rotors), the energy spectrum is given by \( E_J = \hbar Bc \ J(J+1) \) (where \( B = \hbar / 4 \pi I c \) is the rotational constant, \( c \) is speed of light and \( I \) is the molecular moment of inertia). Due to the quantization of the rotational energies, if all of the oscillating terms in equation (1) complete an integer number of \( 2\pi \) in phase, any such wave packet must exactly reproduces itself and indeed it does at integer multiples of the revival time, given by \( T_{rev} = 1/(2Bc) \).

A system is fully described by it’s wavefunction and therefore every \( T_{rev} \), the wavefunction completes a full cycle and regains it's state such that \( \psi(t) = \psi(t + T_{rev}) \).
2.3 Classical - Quantum combination

In what follows, we will combine the classical and quantum mechanical descriptions in order to gain some feeling and predict the angular distribution of the molecular ensemble as a function of time. From the classical description, we have learned that a laser pulse applied to an isotropically distributed molecular ensemble results in molecular angular distribution peaking in the direction of the laser polarization shortly after the pulse. We note this distribution as the “aligned state” or “cigar” due to the shape of the wavefunction in three dimensions (detailed theoretical calculation can be found in section 5.5). In fact, the classical and quantum mechanical descriptions have been previously shown to agree at the close vicinity of the pulse application time $t = 0$[63]. Due to the periodicity of the rotational wavepacket, this aligned state reappears short time after the first $T_{rev}$ and the following revival times. If it was possible to reverse the direction of time in figure 1, the angular distribution would have become perpendicular to the aligned state, namely, the molecules would appear transiently lying in the plane perpendicular to the field polarization.

![Figure 2: propagation of the molecular ensemble shown in figure 1 backwards in time, results in an anti-aligned molecular distribution (left panel). On the background, the corresponding angular distribution in three dimensions is plotted.](image)

This situation is referred to as the anti-aligned or “disk” state. Physically, time reversal is not applicable, but since the classical and quantum mechanical descriptions agree in the vicinity of $t = 0$, and from the phenomenon of quantum revivals, we find the molecular distribution in the anti-aligned state at short times prior to integer revival times. We conclude that at integer multiplications of the revival time, the molecular angular distribution evolves from anti-aligned, through isotropic to aligned state, namely from disk to cigar.

Next, we consider the time evolution of molecular alignment which will be addressed at around key points such as $\frac{1}{2}T_{rev}$ and $\frac{1}{4}T_{rev}$.
We know the time dependence of the eigenstates given in equation (1). However, since our interest is set to the time evolution of molecular alignment, we start with the time dependence of \( \langle \cos^2(\theta) \rangle \) which is the ensemble averaged alignment factor.

Consider the following general rotational wavefunction:

\[
\psi_{(\theta, \phi, \tau)} = \frac{1}{\sqrt{4\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_l^m e^{-i(l+1)\pi\tau} Y_l^m
\]

where: \( \tau = \frac{t}{T_{rev}} \) (2)

A detailed calculation of the coefficients \( c_l^m \) can be found in ref. [84], but at this stage we leave them unspecified for the sake of generality.

The time dependent expectation value of \( \langle \cos^2(\theta) \rangle \) is given by:

\[
\langle \cos^2(\theta) \rangle(\tau) = \langle \psi(\theta, \phi, \tau) | \cos^2(\theta) | \psi(\theta, \phi, \tau) \rangle = \\
\sum_{l,k} \sum_{m} c_l^{m*} c_k^m e^{i(l+1)\pi\tau} e^{-i(k+1)\pi\tau} \left( \frac{1}{A_{lk}} \sum_{B_{lk}} \right) Y_l^m(\theta) \cos^2(\theta) Y_k^m(\theta)
\]

where we average over the contribution of each \( l \), by dividing over it’s multiplicity (number of \( m \) states).

Expression (4) is valid for a wavepacket created by a weak aligning pulse, since it takes into account multiplicity of \( 2l+1 \) \( m \)'s for each \( l \) that is considered. This actually means that no substantial population of \( l \) states that are higher then the initial \( l \) took place.

Let us consider the following cases for \( A_{lk} \) :

### 2.3.1 The \( l = k \) terms:

The contribution of these terms to the alignment factor is time independent since \( A_{lk} = 1 \). What governs the time independent alignment factor is the sum of the \( B_{lk} \) expressions over the relevant \( m \)'s.

\[
\sum_m \sum_l c_l^{m*} c_l^m \left( \frac{1}{2l+1} \right) Y_l^m(\theta) \cos^2(\theta) \frac{1}{2l+1}
\]

Expression (4) is valid for a wavepacket created by a weak aligning pulse, since it takes into account multiplicity of \( 2l+1 \) \( m \)'s for each \( l \) that is considered. This actually means that no substantial population of \( l \) states that are higher then the initial \( l \) took place.
In case of a strong pulse, high $l$ states will be populated but the number of $m$'s does not change since, as claimed before, the operator $\cos^2(\theta)$ does not couple spherical harmonics with different $m$'s. The minimal value for expression (4) is $1/3$ for the isotropic case, whereas the maximal value, for infinitely strong pulse is $1/2$. Intuitively, for infinitely strong pulse, each molecule is forced to rotate in a plane defined by it’s initial molecular axis and the polarization axis, thereby is considered as rotating in 2 dimensions, giving rise to alignment factor of $1/2$.

### 2.3.2 The $l = k \pm 2$ terms:

In this case, the contribution to the alignment factor is time dependent as reflected in the term marked by $A_{lk}$.

$$A_{lk} = e^{i(l+1)\pi \tau} e^{-i(k+1)\pi \tau} = e^{-i(4l+6)\pi \tau}$$  \hspace{1cm} (5)

The maximal amplitude that can be added to the alignment factor is given by term $B_{lk}$. As in the case of $l = k$, these terms can vary between $\frac{1}{3}$ and $\frac{1}{2}$, depending on the pulse strength.

All of the other options for $l, k$ vanish since they are not coupled by the operator $\cos^2(\theta)$.

The analysis of the time dependent alignment factor leans on the phases shown in equation (5) and on the claim stated above regarding the evolution of the alignment factor around the revival times, derived from the classical description and from the quantum revival manifestation above.

The dimensionless time variable $\tau$ in equation (5) goes from $\tau=0$ at the time of laser pulse application, to $\tau=1$ at the first revival time. Since the rotational wavepacket and the corresponding dynamics is periodic, we will focus on one full revival period ($\tau : 0 \rightarrow 1$) as the next revivals are naturally identical.

Taking the derivative of expression (5) with respect to $\tau$ we get:

$$\frac{d}{d\tau} (e^{-i(4l+6)\pi \tau}) = -i(4l + 6)\pi e^{-i(4l+6)\pi \tau}$$  \hspace{1cm} (6)

Expression (6) is the derivative of the time dependent phase (5) with respect to time therefore it reflects the evolution of the wavepacket as a function of time. In what follows we will show that the phase evolution at different times results in the opposite evolution of the alignment factor around different key points of the revival period.
2.4 Alignment factor \(< \cos^2(\theta) > \) around key points during a revival period.

2.4.1 \(< \cos^2(\theta) > \) around \(\frac{1}{2} T_{\text{rev}}\)

The time of half revival corresponds to \(T=\frac{1}{2}\) in our dimensionless calculation.

Compared to \(T=1\), the time dependent phases in expression (5) for \(T=\frac{1}{2}\) are \(\pi\) shifted for all of the \(l's\).

From expression (6), the phase evolution in time is \(\pi\) shifted as well. This means that the alignment factor evolves in reversed order around \(T=\frac{1}{2}\) with respect to its evolution around \(T=1\). An important observation is that all \(l's\) remain “in phase” although shifted by \(\pi\), therefore contribute to the observed alignment factor in a constructive manner.

Indeed, it will be shown later on that this is the case, and the alignment factor around half revival time evolves from alignment, through isotropic distribution towards anti-alignment or from cigar to disk. The fact that around half and full revival the evolution is in the opposite direction is an important result, enabling control and selective addressing of molecular isotopes in a mixture as will be explained in section 5.1.

2.4.2 \(< \cos^2(\theta) > \) around \(\frac{1}{4} T_{\text{rev}}\)

The case of \(T=\frac{1}{4}\) requires a deeper inspection of the phases.

Plugging \(T=\frac{1}{4}\) into expression (5), we get a more complex behavior. By splitting the \(l's\) to even and odd, we find that all even \(l's\) are in phase \(e^{-i(2n+3/2)\pi}\) among themselves (where \(n\) is an integer).

Similarly, the odd \(l's\) are also in phase \(e^{-i(2n+1+3/2)\pi}\). However, the phases of the odd \(l's\) are \(\pi\) shifted with respect to that of the even \(l's\), resulting in a destructive contribution of the odd and even \(l's\) to the observed alignment. Due to nuclear spin symmetry considerations, the relative populations of the even and the odd states is not 1:1, but depends on the atomic nuclear spin and on the statistics it follows (Boson / Fermion), therefore diminished alignment is observed around \(\frac{1}{4} T_{\text{rev}}\) (and \(\frac{3}{4} T_{\text{rev}}\)). This is discussed thoroughly in section 5.2, where we selectively control the rotational excitation in different nuclear spin modifications.

Note that the phases around \(T=\frac{3}{4} T_{\text{rev}}\) are also \(\pi\) shifted with respect to the case of \(T=\frac{1}{4} T_{\text{rev}}\), suggesting that their evolution in time is reversed with respect to each other. This is also discussed and demonstrated in section 5.4.
2.4.3 Alignment factor around higher fractional revivals

Next, we will analyze the case of $\tau=1/8$ which represents all of the other higher fractional revival times. For the sake of simplicity, we will consider only even $l's$, given by $e^{-i(n+3/4)\pi}$. In this case, $n$ is an integer related to the even $l's$ such that $l=2n$ (defined in the previous subsection).

Again, we can easily see that the even $n's$ and odd $n's$ are in phase among themselves but are once again $\pi$ shifted with respect to each other, suggesting that they result in destructive contribution to the observed alignment factor. Going back into the original ladder of $l's$, the states $l=0, 4, 8, 12...$ revive in phase at the time of $\tau=1/8$ and contribute to the alignment factor while the states $l=2, 6, 10, 14...$ revive in phase but contribute negatively to the alignment factor. Since their population ratio even at moderate temperatures is $\sim$1:1, they interfere destructively and their net contribution to the alignment factor is 0. The same claims apply for the two manifolds of the odd $l's$. This unique situation, although absent from the time domain evolution of $<\cos^2(\theta)>$, offers an elegant way for selective excitation of the different manifolds discussed, based on the techniques demonstrated in the publications mentioned above.

The arguments above hold for higher fractional revival times, but by now, the picture should be clear. For a pictorial explanation, we refer the readers to the presentation included in the supplementary material to this thesis. [I will add some ppt slides as supplementary material]

2.5 Theoretical part summary

The analysis performed here enables the (partial) reconstruction of the alignment factor based on the classical molecular behavior in the close vicinity of the ultrashort laser pulse excitation and by the quantized character of the problem. Note that until now, we have not used the actual coefficients $c_{ij}^m$ and the corresponding wavepacket. We have made use of the rather simple classical interaction between the molecular ensemble and the laser pulse, and used the general field free evolution of the rotational wavepacket. It may be interesting to apply this way of thinking to other systems as well.

For complete calculation of the coefficients, we have used an analytical approach described in details in appendix A of section 5.5.

In figure 3 we show a calculation of the alignment factor as a function of time for the case of a homonuclear diatomic molecule with atomic nuclear spins $I=1/2$, calculated separately for odd and even rotational states.
Figure 3. Time dependence of the alignment factor of Nitrogen molecules at room temperature for: (a) even rotational states only, (b) odd rotational states only, and (c) equilibrium 1:3 mixture of odd:even rotational states.

Around full revival ($T_{rev}$), the alignment factor for both even and odd manifolds evolve from anti-alignment to alignment. In vicinity of the half revival time ($1/2 T_{rev}$) the alignment factor evolves in the opposite direction namely from alignment to anti-alignment. However around quarter revival times ($1/4 T_{rev}$, $3/4 T_{rev}$, ...) the even and odd manifolds evolve out of phase: when the even molecules are maximally anti-aligned (i.e. $<\cos^2(\theta)>$ takes the minimal value), the odd molecules are maximally aligned (and vice versa), as was predicted above.

Our experimental results (summarized in published articles) rely on the time dependent evolution at different times along the revival period. By applying a second laser pulse to the (already coherently rotating) molecules, we are able to affect them in various ways. We demonstrate the selective rotational excitation of close molecular species such as nitrogen isotopologues ($^{14}N_2, ^{15}N_2$). We use the out of phase evolution of even and odd states around the quarter revival time for selective excitation of nuclear spin isomers (para and ortho) naturally occurring in all homonuclear diatomics having a non-zero atomic nuclear spin, and we induce field free unidirectional molecular rotation by applying two properly delayed and polarized pulses.
3. Experimental

In the experimental part, I will address the two methods we have used in order to rotationally excite and measure the time dependent alignment factor evolution in time. In both methods, we detect the effect of the molecular angular distribution on the probing laser field due to the change in refractive index expressed by the molecular medium in correlation with the degree of alignment.

3.1 Alignment induced refractive index

The molecular distribution reinforces the index of refraction of the medium through the induced polarization. Consider the case of a single molecule, for which the polarizability components $\alpha_\parallel, \alpha_\perp$ parallel and perpendicular to the molecular axis, significantly differ such that $\alpha_\parallel \gg \alpha_\perp$. If the field polarization is parallel to the molecular axis, the induced dipole is $\mu_{\text{ind}} = \alpha_\parallel E$ (which is the maximal induced dipole) and therefore the polarization will be maximal. On the other hand, if the field polarization is perpendicular to the molecular axis, the induced dipole is $\mu_{\text{ind}} = \alpha_\perp E$ and the polarization will be minimal. The susceptibility is defined as $\chi_e = \frac{P}{E}$ where $P$ is the polarization and $E$ the electric field. $\varepsilon = 1 + 4\pi\chi_e$ is the dielectric permittivity and is related to the refractive index $n \approx \sqrt{\varepsilon}$. It is clear that for an aligned state (cigar), a field polarized parallel to the axis of alignment will experience an increased refractive index $n_{\text{cigar}} > \bar{n}$ while for the anti-aligned (disk) $n_{\text{disk}} > \bar{n}$, where $\bar{n}$ denotes the refractive index of isotropically distributed molecules.
### 3.2 Degenerate Four Wave Mixing (or Transient Grating technique)

Degenerate Four Wave Mixing (DFWM) is a nonlinear optical process in which three input electromagnetic fields are coupled by the third order susceptibility $\chi^{(3)}$ to generate a forth electromagnetic field (the signal). We use the time-delayed degenerate, forward propagating three dimensional phase matched four-wave mixing arrangement[85] in which the generated signal is emitted in a specific direction, obeying photonic linear momentum conservation known also as phase matching.

The third order susceptibility is an 81 terms tensor, where each is a sum of 48 terms, and the signal intensity is proportional to the three input fields $I_{\text{sig}} \propto \chi^{(3)}E_aE_bE_c$. We use 3 degenerate fields (same wavelength and polarization) and therefore the number of terms reduces by a factor of $6(3!)$.

An alternative more intuitive way of thinking about this process is by considering the formation of an intensity grating by two interfering strong fields, and Bragg scattering of the third.

In our experiments, two pulses (pump) are applied simultaneously to the sample such that they temporally and spatially overlap, resulting in the formation of an intensity grating due to their interference. Recall that this intensity grating is applied onto diatomic molecular gas, and can be thought of as being imprinted onto the molecular sample spatially. Only molecules that happen to be at the high intensity areas will be affected (kicked) towards alignment while the others will not be affected at all and will remain angularly isotropic for all times. This forms a space-time dependent refractive index grating. After some delay, a third pulse ($E_c$) is scattered from this intensity grating and if the timing is right, it is diffracted according to the phase matching condition [85] given by $k_s = (k_a - k_b) + k_c$ where $k$ stands for the wave vector of each pulse.

![Time-delayed degenerate, forward propagating, three-dimensional phase matched four-wave mixing arrangement](image)

Figure 4: Time-delayed degenerate, forward propagating, three-dimensional phase matched four-wave mixing arrangement. The two pump fields $E_a, E_b$ arrive simultaneously and $E_c$ is delayed. All 3 fields pass through 3 corners of a rectangle, and the resulting field $E_{\text{signal}}$ is emitted throughout the forth corner.
Even though the probe is applied long after the pump pulses are off, at the fundamental times of molecular alignment (full, half and quarters of the revival time), the probe is diffracted from the revived transient molecular grating.

In the FWM measurement the intensity of the diffracted field is recorded, therefore the phase information of the signal field is lost. In principle, by interfering the signal field with an additional field acting as a local oscillator, the phase of the signal field can be retrieved, also known as heterodyne FWM[86]. In our experiments, we performed a homodyne FWM detection, therefore the difference between cigar and disk (direction of alignment) is not reflected in the signal.

Nevertheless, we have chosen to use this detection scheme for its advantageous feature being highly sensitive due to the zero background measured (null detection). The signal is emitted to a new specific direction away from the incoming laser fields and therefore no filtering or background subtraction is required.

In order to control the molecular rotational excitation, two kicks are needed; therefore, two pairs of excitation pulses are required for the FWM control scheme. To achieve this, we added a second pair of excitation pulses, delayed with respect to the first pair depicted schematically in figure 5.

![Figure 5: Schematic representation of the FWM optical setup. Two pairs of pump pulses (dashed lines) with controlled delay are applied to the gas sample, and a probe pulse (solid line) is scattered off (dotted line) to the detector.](image-url)
3.3 Weak field polarization technique

In this technique, a strong pump pulse, polarized along the \( z \) axis, excites a rotational wavepacket resulting in transient changes of the alignment factor and the corresponding birefringence. A second pulse, much weaker, linearly polarized at a small angle (typically few degrees) to the pump, at a controlled delay. At the times where the molecular angular distribution is anisotropic (alignment or anti-alignment), birefringence is induced in the medium as the refractive index along \( z \), becomes significantly different then the refractive index along \( x \). The second pulse actually probes this birefringence by the change inferred to its initial polarization. This change in polarization is analyzed by a polarizer, set before the detector as is depicted in figure 6.

Figure 6: Weak field polarization technique setup. The pump pulse in the fundamental 800nm laser beam (red). The probing pulse is the second harmonic generated by the SHG crystal. The filters (F) filter out the fundamental 800nm. The probe pulse passes through two polarizers. For maximal co-propagation of the two pulses, we passed them through two telescopes with mutual lense (L3).

In order to understand the polarization changes induced to the probe, we can think of the probing pulse as the sum of two electromagnetic fields of equal frequencies which are polarized along the two axes of the expected birefringence \( x, z \). As long as there is no birefringence in the medium (isotropic molecular distribution) the phases of the two fields accumulated during their propagation remain equal, therefore, when they are added, the resulting polarization of the field remains as it was. However, upon propagation through the birefringent medium, the phases accumulated along the \( x \) and \( z \) axes, may be different, and the polarization resulting in their coherent addition may change. In this case, the polarization change is proportional to the difference in the phases accumulated, thus the difference between alignment and anti-alignment is easily resolved. The described configuration provides a homodyned detection, for which the analyzing polarizer is set at a small angle to the probe’s original polarization, enabling the passing of small background intensity, upon which transient changes are observed. However, by setting the polarizing analyzer perpendicular to the probe polarization, a homodyne signal is recorded, as the background intensity
becomes zero, and any change in the polarization of the probe due to birefringence, results in a positive signal, resembling the case of FWM. In our experiments, the weak field technique was mainly used for comparison with respect to the FWM described before. The advantage of the weak field polarization signal stems from the fact that it reflects the actual birefringence induced in the medium.

Figure 7 presents a comparison between the two optical techniques discussed above. One revival period of $^{14}N_2$ is shown for the homodyne (FWM, upper panel in red) and heterodyne (WFP, lower panel in blue).

![Figure 7: Comparison between the typical signals measured with the two experimental techniques explained above. Upper panel (red) – Four Wave Mixing (homodyne) and lower panel (blue) – Weak Field Polarization (heterodyne). The evolution of the alignment factor through a full revival period is shown.](image)

### 3.4 Laser system

The ultrafast laser system consists of several commercially available components. The heart of the system is a mode-locked Ti : sapphire oscillator (Tsunami) pumped by a CW diode pumped Nd :YVO4 laser (Millennia V). The oscillator produces a train of sub- 35 fs pulses (bandwidth >30 nm FWHM), with a peak wavelength at around 800 nm. The oscillator power was typically 250 mW, which corresponds to <5 nJ per pulse. Next, the weak oscillator pulses are amplified by a chirped pulse regenerative amplifier (CPA) (Spitfire). The pulses are first stretched to about 200 ps, then regeneratively amplified in a Ti : sapphire cavity, pumped by a pulsed Nd :YLF laser [Empower (intracavity second harmonic at ~530 nm)] operating at 1 kHz. The timing of the input of the stretched pulse, and the output of the amplified pulse is controlled by two fast Pockels cells. After the pulse has been amplified and recompressed, its energy is about 0.75 mJ and the repetition rate is 1 kHz.
4. Frequency domain analysis

The two detection schemes described in the experimental part, are performed in the time domain. In both techniques, a probing pulse is applied at a computer-controlled delay to molecular ensemble previously excited by a strong pump pulse (pulse pair in the case of FWM). However, if the time domain signal is Fourier transformed, the resulting spectrum reflects the populations of the wavepacket eigenstates. In this part we will compare the frequency domains of the signals detected in the two experimental methods, used for analyzing our results as they appear in the articles.

4.1 Weak field polarization – Heterodyne detection

In section 2, we considered the time dependence of the alignment factor $< \cos^2 \theta >$ following excitation by an ultrashort laser pulse. In the case of the heterodyned signal (weak field polarization technique), the signal is proportional to:

$$I_{\text{hetero}} \propto [ < \cos^2 (\theta) > - \frac{1}{2} + C ]^2$$

(7)

where $C$ is a constant proportional to the electric probe field [87].

For a pure heterodyne detection, namely for $C$ much bigger than $< \cos^2 \theta >$, the signal intensity becomes proportional to $< \cos^2 (\theta) >$, and clear distinction is observed between the aligned and anti-aligned molecular angular distributions, as they peak in opposite directions (positive and negative respectively).

As for the frequency domain, peaks are observed at frequencies of $(4l + 6)B$ coming from the oscillatory part of the time dependent alignment factor in equation (5).

Figure 8: (a) Typical weak field polarization time domain signal of the alignment factor in nitrogen gas, and the (b) corresponding frequency domain. The peaks correspond to the population of the fundamental rotational states.
The measured signal in figure 8a spans 4 full revival cycles of $^{14}N_2$ rotations, for which $T_{\text{rev}} = 8.3 \text{ ps}$. The aligned and anti-aligned distributions are clearly deciphered, pointing in opposite direction with respect to the background level. Note that in comparison to the calculated signal in figure 3, the signals at $\frac{1}{4}T_{\text{rev}}$ and at $\frac{3}{4}T_{\text{rev}}$ point in the opposite direction. The reason for that stems from the nuclear spin statistics of the nitrogen molecules under investigation. The calculation in figure 3 is performed for the case of $^{15}N_2$ where the atomic nuclear spin ($I = 1/2$) imposes a 3:1 population ratio for odd:even states. In the case of $^{14}N_2$, the atomic nuclear spin ($I = 1$) imposes the bose statistics, resulting in the population ratio of 1:2 for odd:even states. Detailed analysis of the two molecular species may be found in section 5.3.

4.2 Four Wave Mixing – Homodyne detection

In the case of the FWM, the homodyne detection does not distinguish between alignment and anti alignment, and the signal is proportional to:

$$I_{\text{homo}} \propto \langle \cos^2(\theta) \rangle - \frac{1}{2}$$

(8)

In fact, one may think of the homodyne signal as being proportional to the change in refractive index squared $(\Delta n)^2$, where $\Delta n$ is the refractive index change due to the excitation. At the destructive interference sites of this grating, molecules are left isotropically distributed at all times ($\langle \cos^2(\theta) \rangle = \frac{1}{2}$), whereas in the constructive interference sites, the molecules were rotationally excited by the field and their alignment factor and corresponding refractive index, changes with time.

Figure 9: (a) FWM time domain signal from nitrogen molecules and corresponding frequency domain (b).
In the time domain signal in figure 9a, both alignment and anti-alignment signals appear as positive with respect to the zero signal. The frequency domain shown in 9b is significantly different from the frequency domain of the heterodyne measurement (figure 8b), and three distinct regions are observed. In order to correlate the observed peaks to the actual rotational states we go back to the time dependent alignment factor.

In the part dealing with the calculation of the alignment factor (equations 3-5), \( \langle \cos^2 \theta \rangle \) was separated in two parts: a time independent part and a time dependent one. We will need both for the next calculation. The alignment factor as a function of time can be rewritten as follows:

\[
\langle \cos^2 \theta \rangle (\tau) = B_{TI} + \sum_{l,m} B_{TD} c_l^{m*} c_{l+2}^m e^{-i\pi(4l+6)} + c.c \quad (9)
\]

Where \( 1/3 \leq B_{TI} \leq 1/2 \) is the time independent alignment factor, and \( B_{TD} \) are the coupling terms factoring the time dependent terms.

Plugging expression (9) into equation (3) we get the time dependent FWM signal.

\[
I_D(\tau) \propto \delta n^2(\tau) = (\delta B_{TI} + \sum_{l,m} B_{TD} c_l^{m*} c_{l+2}^m e^{-i\pi(4l+6)} + c.c)^2 \quad (10)
\]

\[
= \delta B_{TI}^2 + (10a)
+ 2\delta B_{TI} \left( \sum_{l,m} B_{TD} c_l^{m*} c_{l+2}^m e^{-i\pi(4l+6)} + c.c \right) \quad (10b)
+ \sum_{k,s} \sum_{l,m} B_{TD}^{l,m} c_l^{m*} c_{l+2}^{s} c_k^{s*} c_{k+2}^s e^{-i\pi[4(l+k)+12]} + c.c \quad (10c)
+ \sum_{k,s} \sum_{l,m} B_{TD}^{k,s} B_{TD}^{l,m} c_l^{m*} c_{l+2}^{s} c_k^{s*} c_{k+2}^s e^{-i\pi 4(l-k)} + c.c \quad (10d)
\]

Where \( \delta B_{TI} \equiv B_{TI} - 1/3 \) which is a constant (time independent) change in the alignment factor.

Let us analyze the 4 terms in the expression for the intensity:

(10a) is the time independent change of the alignment factor. This term acts as a local oscillator (LO) field, giving rise to constant intensity throughout the coherent lifetime of the rotational wavepacket.

(10b) this expression if a product of the LO field found in expression (10a) and the sum of oscillating terms. These terms oscillate as the fundamental rotational frequencies \( (4l + 6) \).
(10c) this expression is not factored by the LO field and is actually a sum of terms, oscillating in frequencies, which are the binary sums of the fundamental rotational frequencies. $4(l + k) + 12$

(10d) this expression is very similar to expression (10c) with the exception that the oscillations are at frequencies which are binary differences of the fundamental ones. $4(l - k)$.

Thus, we expect to find 3 regimes in the frequency domain:

**Low frequency region** – where the difference frequencies should be found according to expression (10d). $2\pi t Bc 4(l - k)$.

**Fundamental frequency region** – where the fundamental frequencies should be found according to expression (10b). $2\pi t Bc (4l + 6)$.

**High frequency region** – where the sum frequencies should be found according to expression (10c). $2\pi t Bc (4(l + k) + 12)$.

Note that in figure 9b the fundamental frequency region is not observed, implying that the constant change in alignment factor is very small. Recall that a significant change in the constant alignment factor, requires population transfer to high rotational states which exceeds the thermal population manifold extensively, and may be observed for either low temperatures or intense excitations. Nevertheless, in the part describing our ongoing work on acetylenes (section 7.1), a local oscillator stemming from the formation of plasma will be added to the time independent term and analyzed accordingly.
5. Refereed articles

5.1 Isotope-selective laser molecular alignment (2006)
In this work, we explore and demonstrate selective rotational excitation of one molecular isotope (isotopologue) in a 1:1 mixture of two nitrogen isotopologues, $^{14}N_2$ and $^{15}N_2$. The method is based on interaction of the two species with ultrashort laser pulses set at a specific delay. We explain the requirements for such selective excitation based on the difference in the revival periods of the two. Although demonstrated on isotopologues on nitrogen, we discuss the applicability of this method to any pair of molecular isotopologues, based on their mass ratio, which is clearly a rational number.
Isotope-selective laser molecular alignment

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We experimentally demonstrate isotope-selective alignment in a mixture of $^{14}$N$_2$, $^{15}$N$_2$ isotopes. Following a strong ultrashort laser pulse rotational excitation, the angular distributions of the isotopes gradually become different due to the mismatch in their moments of inertia. At predetermined times, the desired isotope attains an aligned state while the other component is antialigned, facilitating further selective manipulations by polarized light. By a properly timed second laser pulse, the rotational excitation of the undesired isotope is almost completely removed.

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Analysis and separation of molecular species with similar chemical and physical properties continue to be challenging pursuits in physics and chemistry [1]. Isotope separation and isotope ratio determination are well-known examples of this kind. Gaseous diffusion and centrifuge-based separation methods rely on generic mechanical effects caused by small mass differences, but are inefficient and require multiple stages. Laser isotope separation [2], on the other hand, provides high single-stage enrichment, but is molecule-specific, and necessitates tunable narrowband laser sources. A promising separation methodology [3–6] based on laser-induced vibrational wave packets in excited molecular electronic states combines the advantages of the optical and mechanical methods, but still relies on certain spectral selectivity.

Here we introduce a new approach to selective manipulation of multicomponent molecular mixtures, which employs nonresonant laser fields for inducing a drastic contrast between angular distributions of the various species which may eventually lead to their discrimination and separation. In response to strong excitation by an ultrashort laser pulse, all species are transiently aligned [7], and this aligned state is periodically regenerated with molecule-specific periodicity due to the phenomenon of quantum revivals [8–10]. At predetermined later times, the desired species attains an aligned state while other components remain more or less isotropically oriented or are confined to a plane perpendicular to the alignment direction. At these unique times and if significant selective alignment is achieved, an additional linearly polarized laser pulse will preferentially ionize [11,12] or dissociate the selected component leading to its identification or separation. This selective alignment can be controlled by a sequence of pulses, leaving aligned any component “on demand.” We experimentally demonstrate these novel concepts by isotope-selective alignment and judicious rotational control in a mixture of $^{14}$N$_2$, $^{15}$N$_2$ isotopes.

Alignment and orientation of molecules have always intrigued spectroscopists, and provided a wide range of topics to be studied. In the gas phase, molecular alignment following excitation by a strong laser pulse was observed in the 1970s [13], and proposed as a tool for optical gating. In the early experiments, picosecond laser pulses were used for the excitation, and deviation of the refractive index from that of an isotropic gas was monitored as evidence for alignment [14,15]. More recently, these observations have been revisited both theoretically and experimentally (for a recent review, see Ref. [7]). Spatial and temporal dynamics was studied [16–18], and multiple pulse sequences giving rise to enhanced alignment were suggested [19,20] and realized experimentally [12,21–23]. Further manipulations such as the optical molecular centrifuge and alignment-dependent strong field ionization of molecules were demonstrated [24,11,12]. Molecular phase modulators have been shown to compress ultrashort light pulses [25,26] and molecular alignment has been used for controlling high harmonic generation [27–29]. Other experiments were reported where transient grating techniques were used for detailed studies of molecular alignment and deformation [30,31].

The physics of alignment of molecules by ultrashort laser pulses is well understood. A short nonresonant linearly polarized laser pulse induces a molecular dipole moment that in turn interacts with the same electric field. Because of the generally anisotropic molecular polarizability, the laser field delivers a torque to the molecules, causing them to rotate toward the direction of the laser field polarization. A short time after the pulse (a few hundred fs), the angular distribution of molecules elongates along the direction of the field, and the molecular ensemble exhibits (partial) transient alignment under field-free conditions. The aligned angular distribution is symmetrical with regard to the direction of the field (“up” or “down”), leading, for a high degree of alignment, to a cigar shape. In what follows we refer to this geometrical shape as “cigar-like” (see cartoons in Figs. 1 and 2). As time evolves, the molecules lose their alignment. Quantum mechanically, laser pulse excites a wave packet that is formed from many rotational states, and which may be written as

$$|\psi(\theta,t)\rangle = \sum_{J,m} c_{Jm}|J,m\rangle \exp(-iE_Jt).$$  \hspace{1cm} (1)

For linear molecules, the energy spectrum is given by $E_J = hBcJ(J+1)$ (where $B = \hbar/4\pi Ic$ is the rotational constant, $c$ is the speed of light, and $I$ is the molecular moment of inertia). As seen from Eq. (1), any such wave packet exactly reproduces itself at integer multiples of the revival time, $T_{rev} = 1/(2Bc)$. Moreover, as is well known [10], at rational
fractions of the revival time $T_{\text{rev}}$, fractional rotational revivals of the wave packet may also be observed. If it were possible to invert the direction of time, one would observe a strong antialignment (namely a state in which the molecules are in the plane perpendicular to the direction of alignment) just before the applied laser pulse. In what follows, we refer to this “antialigned” state as “disk shaped.” Remarkably, the effect of quantum revivals provides such an opportunity just before the revival time, because $|\psi(\theta,T_{\text{rev}}/2)\rangle = |\psi(\theta,-T)\rangle$.

Thus, every revived cigarlike angular distribution is preceded in time by a disklike state. In addition, it can be shown [19] that in the half-revival domain $(t = t_{\text{rev}}/2)$, the aligned and antialigned states appear in the reversed order.

Following the application of an ultrashort laser pulse to a mixture of different molecules, a sequence of alignment and antialignment revivals is initiated, and at first, for similar species, the periodicity is the same for all components of the mixture (no selectivity at this stage). However, with time, different molecular “clocks” become desynchronized due to the difference in the moments of inertia (and rotational constants), and at well defined times, nonidentical components (i.e., different isotopes) attain angular distributions that may be very different (i.e., cigar versus disk). Any two components of the mixture will have the maximum contrast of their angular distributions if one of them is aligned at exactly the same moment when the other goes through the state of antialignment.

This contrast happens at times when one of the components completes an integer number of revival cycles while the second one performs “an integer and a half” number of its own cycles, i.e.,

$$p T_{\text{rev}}^{(1)} = (q + \frac{1}{2}) T_{\text{rev}}^{(2)} \quad \text{or} \quad (p + \frac{1}{2}) T_{\text{rev}}^{(1)} = q T_{\text{rev}}^{(2)},$$

where $p$ and $q$ are integers. As the ratio of the revival times $T_{\text{rev}}^{(1)}/T_{\text{rev}}^{(2)}$ for different isotopes of the same element is a rational number, Eqs. (2) are linear diophantine equations that may have solutions in positive integers $p$ and $q$. Thus, for nitrogen isotopes $^{14}\text{N}_2$ and $^{15}\text{N}_2$, the revival time ratio is $14/15$, and the suitable solutions are

$$(p,q) = (7,7),(21,22),(35,37), \ldots \ .$$

In this paper, we report the simultaneous alignment and antialignment of two separate isotopic components in a $^{14}\text{N}_2/^{15}\text{N}_2$ mixture as observed by interference of their four-wave-mixing (FWM) signals. We note that molecular alignment is reflected in the increase of the gas refractive index, while the antialignment causes its reduction compared to the isotopic case. We use a time-delayed degenerate, forward-propagating three-dimensional phase-matched FWM arrangement [32], where the first two pulses set up a spatial grating of transiently aligned molecules, and the third, delayed pulse is scattered off this grating. In these experiments, all three input beams (and therefore the fourth output beam as well) were linearly, vertically polarized. The experiments were carried out with $\sim 70$ fs, 200 $\mu$J pulses, from a regeneratively amplified Ti:sapphire laser at 800 nm.

The peak field intensity in the focal region was $3 \times 10^{13}$ W/cm$^2$. Under these conditions, the rotational energy supplied to a nitrogen molecule by the laser pulse is comparable with (and even exceeds) the thermal rotational energy. Based on procedures described earlier [19,33] we estimate the maximal degree of laser-induced alignment to be $(\cos^2 \theta) \sim 0.5$ (compared to the isotropic 0.33). The best antialignment is estimated to be of the order of $(\cos^2 \theta) \sim 0.2$. These estimations are consistent with the results of Refs. [11,22], in which a comparable degree of $N_2$ alignment was directly measured (using Coulomb explosion imaging) under experimental conditions (pulse energy, duration, and focusing) generally similar to ours.

Figure 1 depicts the time-delayed degenerate FWM signal obtained from a single isotope of nitrogen ($^{14}\text{N}_2$) following strong, ultrashort excitation. Over 40 revival cycles, $8.3 \text{ ps}$ each, are observed demonstrating full, half, and quarter revivals. The overall decay of the revivals results from collisions within the cell, and the flight of molecules across the laser beam.

Figure 2(a) shows a full scan over many revivals of 1:1 isotopic mixture of $^{14}\text{N}_2$, $^{15}\text{N}_2$. It shows a much more complicated envelope structure. The most profound features are a dip around $-63 \text{ ps}$ (region $A$) and a peak at $-126 \text{ ps}$ (region $B$). According to our previous analysis [see Eq. (3)], $-63 \text{ ps}$ is the region where $^{15}\text{N}_2$ isotope completes 7 full revival periods while $^{14}\text{N}_2$ performs 7.5 of its own revival cycles. The reversed order of the alignment and antialignment events for these two isotopes causes a pronounced destructive interference in the combined FWM signal [see Fig. 2(b)]. At this time, the sample experiences maximal angular separation of the isotopic components: when one of the isotopes reaches a cigar state, the other one exhibits a disklike angular distribution, and vice versa. This provides a favorable configuration for further manipulation such as selective ionization (or dissociation) of the aligned component by an additional linearly polarized laser pulse. At $-126 \text{ ps}$, the 14th full revival of $^{15}\text{N}_2$ and the 15th full revival of $^{14}\text{N}_2$.
coincide, giving rise to constructive interference (region B). Other combinations of full and fractional revivals give rise to other interference phenomena (regions C and D), and these will be discussed in detail in a forthcoming publication.

As the next step, we consider a “nondestructive” control of molecular alignment by a pair of pulses. A short laser pulse always “kicks” the molecules, delivering torque to rotating wave packets. The response of the molecular ensemble, however, is very sensitive to the timing of the second pulse. If a second pulse is applied at the time of exact revival, its effect is similar to that of the first pulse, namely it kicks the molecules “in phase” with their rotational motion, and adds angular momentum to the already rotating molecules, resulting in a more pronounced alignment. This situation is illustrated by the measurements presented in Fig. 3(a), where the second pulse was applied exactly at $3T_{\text{rev}}$. If, on the other hand, the second pulse is applied at a time of half revival, when the molecules are moving away from alignment, the torque impacted by the second pulse effectively cancels the coordinated motion of the rotating molecules, thwarting any future revivals. This is illustrated in Fig. 3(b), where the second pulse was applied at $2.5T_{\text{rev}}$. These conclusions are also supported by other experiments in which molecular alignment was observed by the weak-field polarization technique [34] and by Coulomb explosion imaging [35].

In the last series of experiments, we used this dramatic difference in excitation response to achieve a two-pulse isotope-selective control in the 1:1 mixture of $^{14}$N$_2$ and $^{15}$N$_2$. As detailed before, at $\sim 63$ ps, $^{14}$N$_2$ completes 7.5 revival cycles while $^{15}$N$_2$ completes 7 revival periods. In this time domain, one of the isotopes is rotating from the disk plane toward the cigar axis, while the other one goes in the opposite direction. A second pulse at that unique time affects the two species very differently. As shown in Fig. 4, the second pulse at $\sim 63$ ps enhances the alignment of $^{15}$N$_2$ molecules, and almost completely stops the rotation of $^{14}$N$_2$ isotopes.

In summary, multiple rotational quantum revivals are observed in molecular isotopic mixtures in response to an impulsive excitation by a short pulse. By utilizing the repetitive nature of the alignment signal, we demonstrate that slight differences in the isotope revival periods give rise to time-resolved discrimination between different isotopic components. Moreover, by observing the destructive interference

![Image](http://example.com/image1)

**Fig. 2.** (Color online) (a) FWM signal from 1:1 $^{14}$N$_2$: $^{15}$N$_2$ mixture (500 torr, room temperature). Destructive interference of full and half revival signals is seen in region A at $\sim 63$ ps; constructive interference of the two full revival signals is observed in region B at $\sim 126$ ps. Interferences of quarter and half revival signals are seen in regions C, D. (b) Enlarged view of the destructive interference region A.

![Image](http://example.com/image2)

**Fig. 3.** (Color online) Alignment signal from $^{15}$N$_2$ gas (300 torr, room temperature), following excitation by two pulses. (a) The two pulses are separated by a multiple of the exact revival time ($3T_{\text{rev}}$). The torque from the second pulse adds coherently to that from the first one, resulting in an observed enhanced alignment signal. (b) The two pulses are separated by an odd multiple of half revival time ($2.5T_{\text{rev}}$). The torque from the second pulse is opposite to the molecular angular velocity, resulting in effective stopping of the rotation.

![Image](http://example.com/image3)

**Fig. 4.** (Color online) FWM signal from 1:1 mixture of $^{14}$N$_2$, $^{15}$N$_2$ (500 torr, room temperature) subject to two pulses (“kicks”), delayed by 63 ps. The first kick excites both molecular isotopes, but the second kick affects them in an opposite way. As a result, after the second kick, only the $^{15}$N$_2$ isotope experiences enhanced temporal alignment as reflected in the periodicity of the signal. The rotational excitation of the second isotope ($^{14}$N$_2$) is almost completely removed.

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the FWM signal from an isotopic mixture, we have identified the specific times when different isotopic species attain drastically different angular distributions. One isotope becomes aligned, while the other lies in the plane perpendicular to the alignment direction. Such a configuration is most favorable for isotope-selective ionization or dissociation by an additional laser pulse, which paves the way to an effective and robust new isotope separation technique. Naturally, for practical schemes of isotope separation one needs a high degree of alignment, which may be achieved, e.g., by multipulse alignment schemes [19,20] that have been already demonstrated experimentally [12,21–23] When more than one pulse is used for the rotational excitation, the exact timing between pulses is crucial. If a second pulse is applied at exact full revival, the rotational alignment is enhanced, whereas if the second pulse is properly applied at the half revival time, the rotational periodic alignment may be effectively stopped. We have further showed that this behavior may be implemented in an isotopic mixture, providing a robust methodology of individually addressing a single component in a mixture, and strongly affecting the rotation of selected species in a mixture.

The ability to selectively address a single species in a multicomponent mixture, and change its physical properties (i.e., alignment, or rotation excitation level), is an important outcome of this work. Based on these observations, one may envisage ultrafast time-resolved analytical methods for isotope ratio determination, identification, and discrimination of close chemical species, and trace analysis. Moreover, selective laser control of molecular alignment/orientation may be efficient in resolving many other general problems in quantum manipulation of multicomponent mixtures [36]. Using the same approach, we have recently realized ultrafast time-resolved isotope composition analysis in a three-component mixture of chlorine isotopes [37]. Further experiments for selective manipulation and spectroscopic distinction between close chemical species such as conformational isomers (conformers) and spin isomers are underway and will be discussed in a forthcoming publication.

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5.2 Selective alignment of molecular spin isomers (2007)

Here we make use of the double pulse control scheme for the selective excitation of molecular nuclear spin isomers (para and ortho). The case of nuclear spin isomers is a more general case of naturally occurring mixtures, and actually is found in all symmetric molecules. In this work we deal with the case of homonuclear diatomics. Based on the pauli principle and the statistics the system follows (depending on the nuclear spin being a boson of fermion), there is a distinct correlation between the nuclear spin symmetry and the rotational symmetry, and in fact, the rotational manipulation is used as a handle for selective rotational excitation of nuclear spin isomers. Theoretical calculations and experimental results for the bosonic case \((^{14}N_2 \; I = 1)\) and for the fermionic case \((^{15}N_2 \; I = 1/2)\) are considered.
Selective Alignment of Molecular Spin Isomers

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We experimentally demonstrate field-free, spin-selective alignment of ortho- and para molecular spin isomers at room temperature. By means of two nonresonant, strong, properly delayed femtosecond pulses within a four wave mixing arrangement, we observed selective alignment for homonuclear diatomics composed of spin 1/2 \( ^{15}\text{N} \) or spin 1 \( ^{14}\text{N} \) atoms. The achieved selective control of the isomers’ angular distribution and rotational excitation may find applications to analysis, enrichment, and actual physical separation of molecular spin modifications.

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According to the Pauli principle, all symmetric molecules having identical nuclei with nonzero spin have distinct nuclear spin isomers [1] that differ by the total spin of the molecular nuclei and the symmetry of the molecular spatial wave function. Alternation in the spectral line intensity in molecular spectra (discovered in 1925 [2]) is a spectacular manifestation of this fundamental concept in quantum mechanics. Spin isomers are known to affect chemical reactions; they can be used as spin labels and can significantly enhance NMR signals [3]. However, the ability to control the ratio of nuclear spin isomers, separate them, or manipulate individual species in a mixture is an extremely challenging task because isomers have almost identical physical and chemical properties. To date, molecular hydrogen is the only substance whose nuclear spin isomers have been relatively easy separated (cryogenically) and used. The low-temperature approach fails for heavier molecules, and the separation of nuclear spin isomers has been demonstrated for only a small number of species [4]. Thus, the search for methods of selective addressing of spin isomers in mixtures continues. Among the promising approaches are laser-based enrichment techniques employing light-induced drift [5,6] and methods of coherent control [6,7].

Recently [8], we demonstrated selective rotational control in a mixture of molecular isotopes (isotopologues), which is based on the different quantum revival times arising from slight differences in isotopic mass. Analyzing the periodic rotational revivals following excitation by a strong ultrashort laser pulse, we identified specific times where one of the isotopic species is aligned along the laser field polarization axis and, at exactly the same time, the other species is antialigned. Such a drastic contrast in the angular distribution allowed us to selectively address only a specific isotopic component and control its rotational dynamics.

In the present Letter, we implement a similar approach to spin isomers, and for the first time experimentally demonstrate laser-induced spin-selective alignment of a single nitrogen spin isomer within a mixture at room temperature. Unlike the isotopes, the different isomers have the same mass composition and therefore are indistinguishable in their revival time. It is the entanglement between the spin and rotational degrees of freedom that allows for the selective rotational control. Following the selective alignment, the aligned species can be identified and selectively ionized [9,10], dissociated, or otherwise addressed by an additional linearly polarized laser pulse, and effectively separated from the rest of the mixture.

Consider a homonuclear diatomic molecule (e.g., \( ^{15}\text{N}_2 \)), composed of two spin 1/2 (Fermionic) atoms. The total molecular wave function should be antisymmetric with respect to the exchange of the identical atomic nuclei. As a result, the spin symmetric (triplet) molecular species populate only odd rotational states (with negative parity), while the antisymmetric (singlet) ones occupy even states. For \( ^{14}\text{N}_2 \) (composed of Bosonic spin 1 atoms), the situation is reversed. When subject to the electric field of a laser pulse, a dipole moment is induced in the molecule, which in turn interacts with the same electric field. The energy of this (second order) interaction is \( V(\theta, t) = -\left\langle \frac{1}{2} \right\rangle e^2(t) \times [(\alpha_\parallel - \alpha_\perp) \cos^2(\theta) + \alpha_\perp], \ \text{where} \ e(t) \ \text{is the envelope of the} \ \text{laser pulse, } \theta \ \text{is the angle between the molecular axis and the (vertical) polarization vector of the field, and } \alpha_\parallel \ \text{and } \alpha_\perp \ \text{are the parallel and perpendicular components of the polarizability tensor, respectively. Since typically } \alpha_\parallel \gg \alpha_\perp, \ \text{the induced dipole is directed along the molecular axis, and the molecule experiences a torque that tends to align it along the laser polarization direction.}

The essential ingredient of our isomer-selective control scheme is the substantial difference in the response of even and odd rotational states to a kick by a strong ultrashort nonresonant laser pulse. Figures 1(a) and 1(b) show the calculated time dependence of the molecular alignment factor, \( \langle \cos^2(\theta) \rangle \) for para and ortho spin isomers. Here, double angular brackets denote quantum averaging and averaging over the initial thermal molecular state. The simulation is done for a 300 K ensemble of “nitrogenlike” molecules in the impulsive approximation (\( \delta \)-kick) that is valid for pulses shorter than the typical time of molecular...
rotation. The impulse imparted to the molecule is characterized by action (kick) strength $P = \left(\frac{1}{2}h\right)(\alpha_{||} - \alpha_{\perp}) \times \int_{-\infty}^{\infty} \psi^2(t)dt$. As seen, both species become transiently aligned shortly after the pulse [11], and this aligned state is periodically regenerated due to quantum revivals [12–14]. The revival period is given by $T_{\text{rev}} = 1/2Bc$ where $B$ is the rotational constant and $c$ is speed of light.

Around full and half revival times, the alignment factors for both para and ortho species evolve in phase, but around quarter-revival times ($\frac{1}{4} T_{\text{rev}}$, $\frac{3}{4} T_{\text{rev}}$, \ldots), the ortho and para isomers evolve out of phase: when the para molecules are maximally antialigned (i.e., $\langle \cos^2(\theta) \rangle$ takes the minimal value), the ortho molecules are maximally aligned (and vice versa). As we have previously shown [8] for isotopes, such an orthogonal alignment of different molecular species makes them amenable to further selective manipulation by a linearly polarized field. For spin isomers (Fig. 1), this favorable situation occurs naturally in each revival cycle due to the spin-rotation entanglement imposed by the Pauli principle. This observation paves the way for laser separation of molecular spin isomers via selective ionization (dissociation) of a preselected species in a mixture. This selectivity stems from the strong dependence of the ionization (dissociation) rate on the angle between the molecular axis and the polarization of the laser [9,10].

If the mixture is excited by two pulses, the torque delivered by the second pulse to the already rotating para and ortho molecules can favor or oppose the molecular rotational motion, depending on the direction of rotation. Thus, the energy $\Delta E_{\text{para}} (\Delta E_{\text{ortho}})$ absorbed by the molecular isomers from a pair of pulses is very sensitive to the delay between them in the quarter-revival domains. Figure 2 depicts the calculated ratio $\Delta E_{\text{para}}/\Delta E_{\text{ortho}}$ (the excitation “selectivity”) as a function of the delay between the pulses. A clear preferential excitation of ortho (para) isomers is seen in the delay regions near $\frac{1}{4} T_{\text{rev}}$ and $\frac{3}{4} T_{\text{rev}}$. For the parameters considered, the rotational energy of the preferentially excited isomer is almost 3 times larger than the thermal energy, while the energy of the other isomer is no more than 20% above its initial thermal value. Once prepared by the properly delayed pair of pulses, the preselected species experiences a sequence of enhanced alignments and antialignments with the $\langle \cos^2(\theta) \rangle$ value of ~0.7 and ~0.1, respectively. At the same time, the other isomer is almost unaffected, and its alignment factor performs small (~0.05) amplitude oscillations around the isotropic value (0.33). The calculation shown in Fig. 2 provides the expected selectivity of 1:18.7 and 1:7.2 for application of the second pulse just before $\frac{1}{4} T_{\text{rev}}$ ($\frac{3}{4} T_{\text{rev}}$) or just after $\frac{1}{4} T_{\text{rev}}$ ($\frac{3}{4} T_{\text{rev}}$), respectively. The resulting dramatic difference in the angular distribution sets the stage for the discrimination between the two isomers.

In our experiments, we implement Time Delayed Degenerate Four Wave Mixing (TD-DFWM) in the forward propagating phase matching arrangement [15] in order to excite, control, and detect molecular alignment. A pair of crossed pulsed laser beams with the wave vectors $k_1$ and $k_2$ creates a transient grating of the refractive index due to the molecular alignment induced by these interfering fields [16–18]. The second pair of laser pulses applied with exactly the same wave vectors at a variable “evolution time” after the first one, modifies this excitation, and the third, delayed pulse is scattered off that coherence, probing the degree of alignment. The experiments were carried out at room temperature with 70 fs, 200 $\mu$J pulses from a regeneratively amplified Ti:sapphire laser at 800 nm. The peak field intensity in the focal region was $3 \times 10^{13}$ W/cm². Under these conditions, the rotational energy supplied to a nitrogen molecule by the laser pulse is comparable with (and even exceeds) the thermal rotational energy. Based on procedures described earlier [19,20], and on a new calibration method which is based on the asymmetry of each of the revived peaks [21] we estimate the
maximal degree of laser-induced alignment to be $\langle \cos^2 \theta \rangle = 0.5$ (compared to the isotropic 0.33), and the best antialignment is estimated to be of the order of $\langle \cos^2 \theta \rangle = 0.2$. These numbers imply a substantial nonperturbative modification of the molecular angular distribution, and are consistent with the reported degree of $N_2$ alignment as measured directly by Coulomb explosion imaging under experimental conditions (pulse energy, duration, and focusing) which are very similar to ours [9,22].

Time domain FWM signals measured in $^{15}$N$_2$ are shown in Fig. 3. In both Fig. 3(a) (red online) and 3(b) (blue online), a pulse applied at $t = 0$ excites rotational wave packets in both spin isomers (ortho and para), and the alternation in intensity resulting from the destructive interference between theortho and para isomers [as depicted in Fig. 1(c)] is clearly visible. After the second pulse (applied around $\frac{1}{4} T_{\text{rev}}$), the revival signals for each isomer are more or less uniform, and the elimination of the alternation in intensities is an indication to the spin-purity of excitation. The ortho to para abundance ratio of 3:1 causes in Fig. 3(a) the ortho signal intensity after the second pulse [3(a)] to be enhanced while the para signal intensity [3(b)] is reduced. The difference stems from the different timing of the 2nd pulse (barely discernible on the time scale of Fig. 3). In 3(a), the second pulse was applied just before, $\frac{1}{4} T_{\text{rev}}$, while in 3(b), it was applied just after (150 fs later).

We further confirm the spin isomer selectivity by complementary analysis of the signal in the frequency domain. The spectrum of the FWM signal contains sum and difference frequency components, $[4(J + J') + 12]Bc$ and $4(J - J')Bc$, of the fundamental rotational frequencies $E_{J+2} - E_J = (4J + 6)Bc$. It is worth mentioning that since the rotational wave packets are excited via a Raman type process ($\Delta J = 0$, $\pm 2$), the parity of populated $J$'s is maintained throughout the entire FWM process.

Figure 4(a) depicts the time domain FWM signal from $^{15}$N$_2$ following a single pulse at $t = 0$. In Fig. 4(b), a second pulse was applied $\sim 150$ fsec after $\frac{1}{4} T_{\text{rev}}$ in order to selectively reduce the excitation of the even rotational states (para-isomers) and enhance the excitation of odd ones (ortho-isomers). Figures 4(c) and 4(d) depict the Fourier transform of the TD-FWM signal in the frequency domain corresponding to the rotational sum-frequency components $[4(J + J') + 12]Bc$. In Fig. 4(c) (single pulse excitation), both even and odd binary sums are present. In Fig. 4(d) (double-pulse excitation), only even sums contribute, indicating that only states of the same rotational parity are coherently populated. The (almost) complete elimination of the odd ($J + J'$) sums provides a convincing indication of the achieved spin selectivity of the excitation. A careful analysis [21] of the experimental data depicted in Fig. 4(d) yields (para to ortho) excitation selectivity of 1:7.1, which is in a good agreement with the calculated prediction of 1:7.2 shown in Fig. 2.

Experimentally, a full time-resolved probe signal trace was recorded for continuously variable delay between the excitation pulses, giving a two-dimensional picture with two temporal axes (see Fig. 5). Then, for every evolution time, the probe trace was Fourier transformed to provide the shown spectrograms, where the tick marks on the horizontal frequency axis are given in terms of the binary sums ($J + J'$).

In Fig. 5(a) (the case of $^{15}$N$_2$), the two horizontal lines (solid and dashed) identify specific evolution times around the $\frac{1}{4} T_{\text{rev}}$ where only $J$ states of the same parity are excited. The dashed line (11.12 psec, just before $\frac{1}{4} T_{\text{rev}}$) corresponds to the selective excitation of para molecules (even $J$ states), and the solid line (11.38 psec, just after $\frac{1}{4} T_{\text{rev}}$) corresponds to the selective excitation of ortho molecules (odd $J$ states). The intensity difference between

![FIG. 3 (color online). Time domain FWM signal from doubly excited $^{15}$N$_2$. The second pulse was applied (a) just before, (b) just after $\frac{1}{4} T_{\text{rev}}$. Note that the second pulse was applied at $\frac{1}{4} T_{\text{rev}}$ (instead of the practically identical time of $\frac{1}{4} T_{\text{rev}}$) to clearly demonstrate the “before” and “after” second pulse signals.](Image 317x150 to 562x268)

![FIG. 4 (color online). Time domain FWM signal from $^{15}$N$_2$ excited by (a) a single pulse and (b) two pulses delayed by $\sim \frac{1}{4} T_{\text{rev}}$. Figures (c) and (d) are the Fourier transforms of (a) and (b), respectively. The depicted $J + J'$ range corresponds to the most intense FWM spectral lines resulting from excitation of the initial thermal ensemble.](Image 54x151 to 298x322)
the two lines stems from population ratio 3:1 for ortho/para isomers of \( ^{15}\text{N}_2 \).

Figure 5(b) presents similar data for \( ^{14}\text{N}_2 \) (two Bosonic atoms with nuclear spin \( I = 1 \)). Here, the Fourier peaks are weak before \( 1 \frac{1}{4} T_{\text{rev}} \) (dashed line, 10.4 psec) and strong after \( 1 \frac{1}{4} T_{\text{rev}} \) (solid line, 10.6 psec). Unlike \( ^{15}\text{N}_2 \), in \( ^{14}\text{N}_2 \) the isomers with symmetric spin wave function occupy the even rotational states and the antisymmetric ones occupy the odd \( J \) states. The equilibrium even/odd population ratio for \( ^{14}\text{N}_2 \) is 2:1.

In conclusion, rotational fractional revivals offer an excellent opportunity to discriminate between spin isomers. For the first time, we demonstrated experimentally spin-selective alignment and rotational control of molecular isomers with the help of double excitation by delayed strong femtosecond laser pulses. The methodology described in this Letter does not require tunable laser sources, does not depend on specific molecular resonance, and may be performed at room temperature. It is thus general and robust and can be applied to most linear molecules. While the current selectivity is already pronounced, further optimization and better selectivity ratio may be achieved by integrating with other recent techniques for molecular rotational control, including enhanced multipulse alignment [19,20,22–25] and shaping of the excitation pulses [26–28]. Moreover, the technique may be potentially extended to nonlinear molecules (like ortho- and para-water, and even larger molecules) by combining it with existing methods for field-free three-dimensional molecular alignment [29–32]. Based on these observations, one may envisage new ultrafast time-resolved analytical methods for discrimination and selective manipulation of molecular spin isomers in multicomponent mixtures and eventually new laser spin isomer separation techniques.

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5.3 Spinning molecules selectively: laser control of isotopes and nuclear spin isomers (2007)

The article was published in a special issue on coherent control, presenting an overview of selective rotational control, starting with the classical picture of laser induced molecular rotation. Some results that where not published previously for the case of Chlorine isotopes (3 naturally abundant) are also discussed.
Spinning molecules selectively: laser control of isotopes and nuclear spin isomers

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Following excitation by a strong ultra-short laser pulse, molecules develop coordinated rotational motion, exhibiting transient alignment along the direction of the laser electric field, followed by periodic full and fractional revivals that depend on the molecular rotational constants. In mixtures, the different species undergo similar rotational dynamics, all starting together but evolving differently with each demonstrating its own periodic revival cycles. For a bimolecular mixture of linear molecules, at predetermined times, one species may attain a maximally aligned state while the other is anti-aligned (i.e. molecular axes are confined in a plane perpendicular to the laser electric field direction). By a properly timed second laser pulse, the rotational excitation of the undesired species may be almost completely removed leaving only the desired species to rotate and periodically realign, thus facilitating further selective manipulations by polarized light. In this paper, such double excitation schemes are demonstrated for mixtures of molecular isotopes (isotopologues) and for nuclear spin isomers.

1. Introduction

Alignment and orientation of molecules have always intrigued spectroscopists, and provided a wide range of topics to be studied. In the gas phase, molecular alignment following excitation by a strong laser pulse was observed in the 1970s [1] and proposed as a tool for optical gating. In the early experiments, picosecond laser pulses were used for the excitation, and deviation of the refractive index from that of an isotropic gas was monitored as evidence for alignment [2, 3]. More recently, these observations have been revisited both theoretically and experimentally (for a recent review, see [4]). Spatial and temporal dynamics was studied [5–7] and multiple pulse sequences giving rise to the enhanced alignment were suggested [8, 9] and realized [10–13]. Further manipulations such as the optical molecular centrifuge and alignment-dependent strong field ionization of molecules were demonstrated [13–15]. Molecular phase modulators have been shown to compress

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ultrashort light pulses [16, 17] and molecular alignment has been used for controlling high harmonic generation [18–20]. Other experiments were reported where transient grating techniques were used for detailed studies of molecular alignment and deformation [21, 23].

Analysis and separation of molecular species with similar chemical and physical properties continue to be challenging pursuits in physics and chemistry [23]. Since separation is based on differences in one or more physical or chemical properties, selective manipulation is becoming increasingly more difficult as the species become more and more alike. In the case of isotopologues (chemical species that differ only in the isotopic composition of their molecules), the difference lies in the nuclear mass of the different species (and therefore also in their moment of inertia and rotational constant), whereas for spin isomers, the mass is the same, and the difference is in the response to an external magnetic field and in the symmetry properties of the entire molecular wavefunction describing the state.

Here we introduce a new approach to selective manipulation of multi-component molecular mixtures. By employing non-resonant laser fields, we induce drastic transient contrasts between the angular distributions of the various species. These differences should eventually lead to their discrimination and separation.

We start with a detailed description of the molecular evolution following the application of a laser pulse, and we focus our attention on the coherent rotational motion manifested in a transient angular distribution.

When molecules with a permanent dipole moment (such as HCl, KI etc.) are subject to a DC electric field, they align parallel to the applied field direction. The torque exerted on a molecule is proportional to the component of the field perpendicular to the molecular axis. A related effect is achieved with molecules without a permanent dipole moment such as I₂, CO₂, N₂ etc. When a laser pulse acts on such a molecule, it induces an electric dipole through the anisotropic molecular polarizability tensor, which in turn interacts with the electric field. This second-order interaction aligns the molecules along the external field as well.

Let us consider an ensemble of polarizable molecules in the gas phase, possessing an isotropic initial angular distribution. A typical rotational time for a small molecule is of the order of several picoseconds, therefore with femtosecond pulse duration, the molecule can be regarded as frozen during the pulse. When a strong femtosecond laser pulse is applied, each molecule gains angular velocity depending on the angle \(\theta\) between the molecular axis and the laser pulse polarization direction (see figure 1). The molecules start rotating towards the electric field direction immediately after the pulse, however a significant reorientation will be noticed only after the pulse is over, i.e. under field-free conditions [24]. During the pulse, every molecule experiences a torque which is proportional to the square of the projection of the field on the molecular axis. Assuming no initial rotational velocity prior to the pulse, a molecule at the angle \(\theta\) will gain the angular velocity \(\omega(\theta) \propto -P \sin(2\theta)\) (where \(P\) can be considered as the ‘strength’ of the pulse given by \(P = \int_{-\infty}^{\infty} \varepsilon(t) \, dt\)). According to this argument, a molecule which is oriented at \(\theta = \pi/4\) to the field, will gain the highest angular velocity towards the field direction, whereas a molecule oriented perpendicular to the field \((\theta = \pi/2)\), will gain no angular velocity. After the pulse, the molecules rotate according to their new angular velocity.
and short time after the pulse (several hundreds of femtoseconds) the distribution will have a peak in the direction of the field, a state that we refer to as the 'aligned state' or 'cigar'. This state is manifested in the increase of the refractive index for light polarized in the direction of the aligning pulse [25].

Quantum-mechanically, a laser pulse excites a wave packet which is formed from many rotational states ($J$'s), and which may be written as

$$|\psi(\theta, t)\rangle = \sum_{J,m} c_{J,m} |J,m\rangle \exp(-iE_Jt/\hbar).$$

(1)

For linear molecules, the energy spectrum is given by $E_J = hBc\, J(J + 1)$ (where $B = h/4\pi Ic$ is the rotational constant, $c$ is speed of light and $I$ is the molecular moment of inertia). As can be seen from equation (1) any such wave packet exactly reproduces itself at integer multiples of the revival time, $T_{\text{rev}} = 1/(2Bc)$ (quantum revivals phenomenon [26–28]). Shortly before the realignment revival, the molecules attain a state of ‘anti-alignment’, namely a state where the molecular axes are confined in the plane perpendicular to the direction of alignment. In what follows, we refer to this ‘anti-aligned’ state, as ‘disc’ shaped, which is also accompanied by a reduction in the refractive index along the polarization axis of the aligning pulse. Thus, every revived cigar-like angular distribution is preceded in time by a disc-like state (shown in figure 2). In addition, it can be shown [8] that around the half-revival time ($t \approx T_{\text{rev}}/2$) the aligned and anti-aligned states appear in the reversed order. In between these special times, the molecules lose their macroscopic alignment and assume an almost isotropic angular distribution until the next revival event.

During its evolution, the rotational wave packet also exhibits other partially aligned and anti-aligned distributions at quarter and three quarters of the revival time. These are not as pronounced as the full and half revival times, due to internal destructive interferences between the odd and even rotational states.

Figure 1. A laser pulse interacting with a diatomic homonuclear molecule. The torque exerted on the molecule is proportional to $-\sin(2\theta)$, where $\theta$ is the angle between the laser pulse polarization and the molecular axis. (The colour version of this figure is included in the online version of the journal.)
2. Experimental

We use a time-delayed degenerate, forward propagating, three-dimensional, phase-matched four-wave mixing arrangement [29], where the first two pulses set up a spatial grating of transiently aligned molecules, and the third, delayed pulse is scattered off this grating. In these experiments, all three input beams (and therefore the fourth output beam as well) were linearly, vertically polarized. The experiments were carried out at room temperature with 70 fs, 200 μJ pulses from a regeneratively amplified Ti:sapphire laser at 800 nm. The peak field intensity in the focal region was $3 \times 10^{13} \text{ W cm}^{-2}$. Under these conditions, the rotational energy supplied to a nitrogen molecule by the laser pulse is comparable with (and even exceeds) the thermal rotational energy. Based on procedures described earlier [8, 30] we estimate the maximal degree of laser-induced alignment to be $\langle \cos^2 \theta \rangle \approx 0.5$ (compared to the isotropic 0.33). The best anti-alignment is estimated to be of the order of $\langle \cos^2 \theta \rangle \approx 0.2$. These estimations are consistent with the results of [11, 15], in which a comparable degree of N$_2$ alignment was directly measured (using Coulomb explosion imaging) under experimental conditions (pulse energy, duration and focusing) generally similar to ours.

Figure 3 depicts the time delayed degenerate FWM signal obtained from a single isotope of nitrogen (14N$_2$) following strong, ultrashort excitation. Over 40 revival cycles, 8.3 ps each, are observed, demonstrating full, half and quarter revivals. The overall decay of the revivals results from collisions within the cell, and the flight of molecules across the laser beam.

Next we consider control of molecular alignment by a pair of pulses. A single short laser pulse ‘kicks’ the molecules, thus generating a rotational wave packet. However, in a double pulse excitation, the response of the molecular ensemble is very sensitive to the timing of the second pulse. If a second pulse is applied at the time of exact revival, its effect is similar to that of the first pulse, namely it kicks the
molecules ‘in phase’ with their rotational motion, and adds angular momentum to the already rotating molecules, resulting in a more pronounced alignment. This situation is illustrated by the measurements presented in figure 4(a). When the second pulse is applied exactly at $3T_{\text{rev}}$, the amplitude of the alignment peaks seems to increase significantly. If, on the other hand, the second pulse is applied at the time of half revival, when the molecules are moving away from alignment, the torque impacted by the second pulse effectively cancels the coordinated motion of the rotating molecules, thwarting any future revivals. This is illustrated in figure 4(b), where the second pulse was applied at $2.5T_{\text{rev}}$. These conclusions are also supported by other experiments in which molecular alignment was observed by weak field polarization technique [31] and by Coulomb explosion imaging [32].

2.1 Selective rotational excitation of isotopologues

Gaseous diffusion and centrifuge-based isotope separation methods rely on mechanical effects caused by small mass differences. They are rather general, but relatively inefficient and require multiple separation stages. Laser isotope separation [33] on the other hand, provides high single-stage enrichment, but is molecule-specific, and since done in the frequency domain, it necessitates tunable narrow-band laser sources. A promising separation methodology [34–37] based on laser-induced vibrational wave packets in excited electronic states has been demonstrated, combining the advantages of the optical and mechanical methods, but it still relies on certain spectral selectivity. In what follows, we consider non-resonant isotope-selective rotational control in a mixture of different molecular isotopes of the same chemical element [38].

Figure 3. Long scan FWM signal from N$_2$ gas (200 torr, room temperature). 40 full revival cycles are shown (~320ps), where quarter, half and full revivals are clearly seen. The inset depicts one full revival cycle. Although the FWM signals around full and half revival seem similar, the corresponding angular distributions are reversed [8]. (The colour version of this figure is included in the online version of the journal.)
Following the application of an ultrashort laser pulse to a mixture of different molecules, a sequence of alignment and anti-alignment revivals is initiated. For similar species the periodicity is almost the same for all components of the mixture (no selectivity at this stage). However, as time propagates, different molecular ‘clocks’ become desynchronized due to the difference in their moments of inertia (and rotational constants), and at well-defined times, non-identical components (i.e. different isotopes) attain angular distributions which may be very different (i.e. cigar versus disc).

We utilize the periodic behaviour of the rotational wavepackets and the desynchronization discussed above for the specific addressing of molecular isotopologues too similar to be resolved on shorter time scales. As an example we use the homonuclear diatomic chlorine molecules, consisting of various mixtures of two natural isotopes $^{35}\text{Cl}$ and $^{37}\text{Cl}$, giving rise to three molecular species: $^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$, $^{37}\text{Cl}^{37}\text{Cl}$. Due to the (small) differences in their moments of inertia, the isotopic species will display very close revival periods. Consider two molecular isotopes with revival periods such that their (small) difference is given by $t_{\text{rev}}^1 - t_{\text{rev}}^2 = \Delta \tau$. After one revival period the alignment signals of the two isotopes will be separated by $\Delta \tau$, but after N cycles the difference will accumulate to $N \Delta \tau$, and the two species may be temporally resolved. In a set of experiments, we observed multiple revivals in chlorine gas. The known rotational constants of these molecules correspond to a revival time of $\sim 68$ ps. At the first half and full revivals the signal from the different isotopes are too close to be resolved (figure 5(b)), but at the second full revival ($\sim 140$ ps) (figure 5(c)) the contributions of the three different isotopic

![Figure 4. Alignment signal from $^{15}\text{N}_2$ gas (300 torr, room temperature), following excitation by two pulses. (a) The two pulses are separated by a multiple of the exact revival time ($3 t_{\text{rev}}$). The torque from the second pulse adds coherently to that from the first one, resulting in enhancement of alignment signal. (b) The two pulses are separated by an odd multiple of half revival time ($2.5 t_{\text{rev}}$). The torque from the second pulse is opposite to the molecular angular velocity, resulting in effective stopping of the rotation. (The colour version of this figure is included in the online version of the journal.)](image-url)
species are separated by about 4 ps and are clearly and fully resolved. Note that based on the generic explanation leading to figure 2, the signal from each isotope should have been a simple doubled peak. The deviation from this simple picture and the weaker ‘extra’ peaks arise from the centrifugal distortion of higher rotational states.

In order to selectively manipulate a single species in a bimolecular mixture, we look for time windows where the contrast between the two components is maximal. Any two components of the mixture will have the maximum contrast of their angular distributions when one is aligned at exactly the same moment when the other goes through the state of anti-alignment. This contrast is found at times when one of the components completes an integer number of revival cycles while the second one performs ‘a half integer’ number of its own cycles, i.e.

\[ pT_{\text{rev}}^{(1)} = \left( q + \frac{1}{2} \right) T_{\text{rev}}^{(2)}, \quad \text{or} \quad \left( p + \frac{1}{2} \right) T_{\text{rev}}^{(1)} = qT_{\text{rev}}^{(2)}, \]  

(2)

where \( p \) and \( q \) are integers. As the ratio of the revival times \( T_{\text{rev}}^{(1)}/T_{\text{rev}}^{(2)} \) for different isotopologues of the homonuclear diatomic molecule is a rational number,
equations (2) are linear Diophantine equations that may have solutions in positive integers \( p \) and \( q \). Thus, for nitrogen isotopologues \(^{14}\text{N}_2\) and \(^{15}\text{N}_2\), the revival time ratio is \(14/15\), and the suitable solutions are

\[
(p, q) = (7, 7), (21, 22), (35, 37), \ldots
\]  

Figure 6 depicts a measurement of the simultaneous alignment and anti-alignment of two isotopic components in a \(^{14}\text{N}_2^{15}\text{N}_2\) mixture as observed by the interference of their four-wave mixing (FWM) signals. Note that molecular alignment is reflected in the increase of the gas refractive index, while the anti-alignment causes its reduction compared to the isotropic case.

Figure 6(a) shows a full scan over many revivals of the 1:1 mixture of \(^{14}\text{N}_2^{15}\text{N}_2\). Compared to the single component picture (figure 3) it shows a much more complicated envelope structure. The most profound features are a dip around \(\sim 63\) ps (region A) and a peak at \(\sim 126\) ps (region B). According to our previous analysis (see equation (3)), \(\sim 63\) ps is the region where the \(^{15}\text{N}_2\) isotope completes 7 full revival periods while \(^{14}\text{N}_2\) performs \(7\frac{1}{2}\) of its own revival cycles. The reversed order of the alignment and anti-alignment events for these two isotopes causes a pronounced destructive interference in the combined FWM signal (see figure 6(b)). At this particular time, the sample experiences maximal angular separation of the isotopic components: when one of the isotopes reaches a cigar
state, the other one exhibits a disc-like angular distribution, and vice versa. This provides a favourable configuration for further manipulation such as selective ionization (or dissociation) of the aligned component by an additional linearly polarized laser pulse. At \( t = 63 \) ps, the 14th full revival of \(^{15}\text{N}_2\) and 15th full revival of \(^{14}\text{N}_2\) coincide, giving rise to constructive interference (region B). Other combinations of full and fractional revivals give rise to other interference phenomena (regions C and D), and these will be discussed in detail in the next section, dealing with spin isomers.

We used this dramatic difference in angular distribution to achieve a two-pulse isotope-selective control in the 1:1 mixture of \(^{14}\text{N}_2\), \(^{15}\text{N}_2\) (500 torr, room temperature). As detailed, at \( t = 63 \) ps \(^{14}\text{N}_2\) completes 7.5 revival cycles while \(^{15}\text{N}_2\) completes 7 revival periods, one of the isotopes is rotating from the disc plane towards the cigar axis, while the other one goes in the opposite direction. A second pulse at this time would affect the two species very differently. As shown in figure 7, the second pulse at \( t = 63 \) ps enhances the alignment of \(^{15}\text{N}_2\) molecules, and almost completely stops the rotation of \(^{14}\text{N}_2\) isotopes!

Figure 7. FWM signal from 1:1 mixture of \(^{14}\text{N}_2\), \(^{15}\text{N}_2\) (500 torr, room temperature) subject to two pulses (‘kicks’), delayed by 63 ps. The first kick excites both molecular isotopes, but the second kick, affects them in an opposite way. As a result, after the second kick, only the \(^{15}\text{N}_2\) isotope experiences enhanced temporal alignment as reflected in the periodicity of the signal. The rotational excitation of the second isotope (\(^{14}\text{N}_2\)) is almost completely removed. (The colour version of this figure is included in the online version of the journal.)

Up to this point, we have discussed the cases of mixtures of chemical species having close mechanical properties. We made use of the periodic evolution of their angular distributions and have shown that they can be distinguished spectroscopically with the aid of their rotational quantum revivals. We have demonstrated the selective rotational excitation using a double pulse scheme, of a single component and in bimolecular mixture, and briefly discussed the potential for physical separation of such mixtures by selective dissociation/ionization upon application of another laser pulse at specific times where the different components assume dramatically different angular distributions.
The case of spin isomers

In the case of isotopologues we made use of the slight difference in the moment of inertia arising from the difference in masses of their atomic constituents. In the case of spin isomers, such a difference is not found. The chemical and physical properties of spin isomers are similar and, in fact, the only difference between the spin isomers is their response to the gradient of external magnetic field as in the case of the Stern–Gerlach experiment. Therefore, the ability to control their ratio in a mixture is not a simple task. A few practical applications of spin isomers are already known. For example, spin isomers can affect chemical reactions [39, 40], can significantly enhance NMR signals [41, 42] or can be used as spin labels in NMR-based techniques.

Linear symmetric molecules whose atomic constituents possess a non-zero nuclear spin exist as either ortho or para spin isomers, differing in the symmetry of their nuclear states. For a homonuclear diatomic molecule of spin 1/2 atoms, the total nuclear spin can be \( I = 1 \) (ortho molecule), or \( I = 0 \) (para molecule). This difference in symmetry implies statistical differences in the population of even and odd rotational states. Since spin changing collisions or radiational transfers are forbidden by symmetry, these species are rather stable, and once prepared can be used and stored for long times. At low temperatures, ortho and para molecules can be in principle separated based on the statistics they follow (Fermi–Dirac/Bose–Einstein) but in practice, this has been applicable only for the lightest of all molecules, hydrogen.

Consider a spin 1/2 homonuclear diatomic molecule (e.g. \(^{15}\)N\(_2\), H\(_2\)). Different spin quantum number combinations give rise to different symmetries of the rotational part of the wavefunction. For a spin 1/2 atom in a homonuclear diatomic, the spin symmetric molecular species populate the odd rotational states and the antisymmetric ones populate the even state as presented in figure 8. In the case of a spin 1 atom, the

![Figure 8. The four diatomic molecular spin isomer species, for a homonuclear diatomic molecule of spin 1/2 atoms. The spin function symmetry and corresponding rotational state parity for the spin 1/2 atom case are shown, from which one can see that the symmetric (odd J) species are three times more abundant. (The colour version of this figure is included in the online version of the journal.)](image-url)
correlations between the symmetry and the rotational state parity is reversed due to the difference in the behaviour of fermions and bosons. The difference in the parity of rotational states populated by the different spin isomers provides the key for their selective manipulation and in fact, the problem of selective excitation of spin isomers is reduced to selective excitation of even or odd rotational states.

In order to establish the connection between the $J$ state parity and the angular distribution, we should remember that around full revival times all species behave similarly, evolving from the anti-aligned ‘disc’ state through the isotropic state to the aligned ‘cigar’ state, and at half revival they follow the reversed order [43]. As an illustration, the alignment factor ($\langle \cos^2 \theta \rangle$) during one full revival period for even and for odd states is depicted in figure 9.

As noted, around half and full revivals the odd and even states behave similarly, but around quarter revivals ($\frac{1}{4}$, $\frac{3}{4}$) they evolve in reversed orders such that around $\frac{1}{4} T_{\text{rev}}$, the odd $J$ states reach an anti-aligned (‘disc’) state while the even $J$ states reach an aligned state (‘cigar’). Around $\frac{3}{4} T_{\text{rev}}$, they ‘switch their roles’ such that the even $J$’s go through the disc state while the odd ones assume a cigar angular distribution. A second pulse applied around these times would affect the different parity rotational states (and corresponding spin isomers) in opposite ways. In a manner similar to the situation described in figure 4 above, the torque applied by the second pulse may either consent or oppose the already rotating molecules, depending on the exact timing and the sense of rotation.

We use the same experimental setup already described in the previous section. It is worth noting that since the excitation is a Raman-type process ($\Delta J = \pm 2$), it maintains the $J$ state parity distribution, meaning that a molecule initially occupying even (odd) states, will maintain its state parity occupation after the interaction with the laser pulses. Since the experimental time domain data is analysed in its Fourier space, we begin with a brief review of the main points of frequency domain CARS. A detailed theoretical analysis of the frequency domain is included in a forthcoming publication.

3. Frequency domain analysis—test case

In FWM experiments the signal intensity is proportional to the square of the induced polarization, or in the language of transient gratings, the scattering intensity is
proportional to the refractive index grating written by the two initial laser pulses. For this reason, both the aligned (high n) and the anti-aligned (low n) states will give rise to positive FWM signals. This is a marked difference from linear measurements where the actual sense of the change in refractive index may be observed, and positive as well as negative signals are observed. Fourier analysis of this ‘positive definite’ time delayed FWM signal results in an unusual frequency domain signature where binary sums and differences of the populated rotational states are observed.

As an example for this frequency domain analysis, let us examine the FWM signal from $^{15}$N$_2$ subject to a single excitation event.

Figure 10(a) depicts the time delayed signal from $^{15}$N$_2$ subject to a single pulse and its full range Fourier transform is depicted in figure 10(b). One can easily notice two regions, low and high frequencies corresponding to binary differences and sums of the populated $J$ states. Since the nuclear spin of $^{15}$N is $\frac{1}{2}$, the atoms should follow the Fermi–Dirac statistics and the expected even/odd population ratio is: $[J_{odd}/J_{even}] = (I + 1)/I = 3:1$.

In the low frequency regime (figure 10(c)) we expect to find frequencies coming from binary differences of $J$ states. If we denote such binary differences by $d$, one notes immediately that even $d$ peaks are generated by $J$ states of same parity whereas odd $d$ peaks are generated by $J$ states of different parity.

Inspection of figure 10(c) reveals that the peaks at even $d$ are higher than those at odd ones. Moreover, simplistically, one would have expected the $d=1$ peak to be of the highest intensity (since it involves all neighbouring $J$ states), but instead, the $d=2$ peak is stronger. Both observations are explained by the fact that the even states are three times more populated than the odd states.

In the high frequency region (figure 10(d)) we find frequencies arising from binary sums of the populated $J$ states. If we denote such binary sums as $s$, one notes immediately that even $s$ peaks are generated by $J$ states of the same parity whereas odd $s$ peaks are generated by $J$ states of different parities. As in the low frequency region, here, too, the peaks at even $s$ are higher, and for exactly the same reason.

Next we move forward to discuss double pulse schemes, where selective excitation is implemented.

4. Selective excitations of para/ortho spin isomers

Our selective excitation scheme is based on the laser excitation of all components in the mixture, followed by wavepacket evolution and the application of a second pulse at a time when the angular distributions of the two species evolve in opposite directions. This happens around quarter and three quarters of the revival time for spin isomers.

We start with a comparison of single and double pulse excitations of $^{15}$N$_2$ in figure 11.

Figure 11(a) depicts the time domain FWM signal from $^{15}$N$_2$ following a single pulse at $t=0$. The horizontal axis is marked in units of revival times, so the large peaks correspond to full and half revivals, whereas the low intensity peaks at quarter...
revivals ($\frac{1}{4}$ and $\frac{3}{4} T_{\text{rev}}$) result from destructive interference of even and odd $J$ states. In figure 11(b), a second pulse was applied around $\frac{3}{4} T_{\text{rev}}$, at the right time to decrease the intensity of the even rotational states and enhance the rotation of the odd state. In figure 11(b) the interference is greatly reduced as is evidenced by the more or less constant intensity of the peaks. Note also that the intensity of the peaks observed after the second pulse is higher than the intensity of the peak before the second pulse. This is a consequence of the 3:1 odd/even population ratio in the case of $^{15}$N$_2$ (see figure 7 and the discussion that follows). Figure 11(c) and (d) depict the frequency region corresponding to binary sums of rotational states (‘high frequency region’).
The fact that only the even sums of $J$ states are observed indicates that only states of the same parity (even or odd), are coherently populated. The same effect is seen in the low frequency region, where only even differences of $J$ states are observed (not shown here).

In order to drive the system towards the desired goal of selective excitation of only one of the components in the mixture, the second excitation pulse should be applied at exactly the time when the two constituents are evolving out of phase. From the theoretical prediction in figure 9 we know that there are two such points around $\frac{1}{4}(\frac{3}{4})T_{\text{rev}}$, but the exact time depends on several additional parameters such as the temperature, and pressure and most important, the pulse duration. To find this exact time, we scan both the delay between the two excitations (the time between the two pairs of pulses, also referred to as ‘evolution time’) and the probe pulse (scanning one full revival time $\sim 10$ ps after the second excitation pulse, for each evolution time). The results of these two-dimensional scans are depicted in figure 12.

Figure 12(a) presents the time domain two-dimensional plot where the horizontal axis is the probe delay, measuring the reviving rotational alignment peaks, and the vertical axis is the delay between the exciting pairs around the $T_{\text{rev}} = \frac{3}{4}$ time. Figure 12(b) is the line by line Fourier transform of figure 12(a), showing the spectrum of the excited rotational state (marked in actual rotational numbers) for the given evolution times on the vertical scale.

The two horizontal lines in figure 12(b) identify two specific time delays around the $\frac{3}{4}T_{\text{rev}}$ (dashed, solid) where $J$ states of single parity are excited (indicated by the even sums). The dashed line (intersecting the vertical axis at 6650 fs) corresponds to selective excitation of the even states (populated by only para molecules), and the solid line (intersecting the vertical axis at 6880 fs) corresponds to selective excitation...
of odd \( J \) states (populated by only ortho molecules). The intensity difference between the two time delays stems from the ortho/para population ratio (3:1, respectively). As discussed above, these unique time delays appear just before and after the exact time of alignment, when the angular distribution evolves from ‘disc’ to ‘cigar’ for enhancement (or in the reversed order for reduction) of the rotational energy. An equivalent behaviour is observed for \(^{15}\text{N}_2\) around \( \frac{1}{4} T_{\text{rev}} \) (figure 13(a)) with a reversed order of the molecular response.

These same effects are also observed for \(^{14}\text{N}_2\). The nuclear spin of \(^{14}\text{N}\) is 1, thus \(^{14}\text{N}_2\) obeys Bose statistics and the resulting para/ortho (even/odd \( J \) states)
ratio is 2/1. The population ratio does not affect the qualitative behaviour of the even and odd states but it is reflected in the details of the Fourier transform. This difference in nuclear spin also affects the correspondence between the $J$ states parity and the symmetry of spin isomers. Unlike the case of the fermionic $^{15}\text{N}_2$, in $^{14}\text{N}_2$ the symmetric spin wavefunctions occupy the even $J$ states and the antisymmetric ones occupy the odd ones. The bottom line of these differences is that the temporal behaviours of the two molecules are exactly complementary, as may be seen in figure 13. The figure depicts a comparison between the 2D Fourier transforms of these two species, where the interpulse delay in the double pulse excitation scheme was around $\sim 1 \frac{1}{4} T_{rev}$.

From the comparison between the 2D FFT of the $^{14}\text{N}_2$ (right) and $^{15}\text{N}_2$ (left), one can clearly see the difference in the ratio of peak intensities at the dashed and solid lines. While in the case of $^{15}\text{N}_2$ the ortho/para (odd/even $J$'s) is 3:1, for $^{14}\text{N}_2$, the ratio of para/ortho (odd/even $J$'s) is 1:2. The behaviour of the $J$ states remains the same but the relative population ratio and correlated spin isomers are changed. For a second pulse excitation which is applied around $\frac{3}{4} T_{rev}$ (not shown), the intensities in each plot interchange with respect to the timing of the second pulse. Furthermore, if we compare the case of $^{15}\text{N}_2$, $1 \frac{1}{4} T_{rev}$ (figure 13(a)) to the $^{15}\text{N}_2$, $\frac{3}{4} T_{rev}$ (figure 12(b)) the intensities of the peaks are also reversed, as expected (see figure 9).

5. Summary

In summary, multiple rotational quantum revivals are observed in molecular isotopic mixtures in response to an impulse excitation by a short pulse. By utilizing the repetitive nature of the alignment signal, we have shown that slight differences in the isotopes’ revival periods give rise to time-resolved discrimination between different isotopologues (Cl$_2$, N$_2$). Since the ratio between the isotopologues’ masses (and corresponding moments of inertia) is a rational number, one can easily calculate a time when the species to be separated reach a maximal difference between their angular distributions. At this time, one component evolves from disc to cigar (full revival time) distribution while the other evolves in the reversed direction (half revival time), setting the conditions for their selective excitation. A second laser pulse applied at that time results in the alignment enhancement for one component and decrease for the other one. Around this specific time, a dramatic difference exists in the angular distributions, and thus an opportunity arises for preferred ionization or dissociation of one or the other component. In the last part, we applied the double pulse scheme for selective excitation of spin isomers. In this case, there is no difference in the moment of inertia between the para and ortho isomers, therefore they revive at exactly the same times, and cannot be separated on a temporal basis.

We have identified and demonstrated the difference in the behaviour of ortho and para species around the quarter and three quarters revival times which is based on the different statistics they follow (Fermi–Dirac/Bose–Einstein), and the corresponding $J$ state occupation, leading to the maximal difference in their angular distributions around these times. Here, too, the second pulse affects the molecules in
opposite ways; stopping the rotation of one component while enhancing it for the other.

The ability to selectively address a single species in a multi-component mixture, and change its physical properties (i.e. alignment, or rotation excitation level) is the main result of this work. Based on these observations, one may envisage ultrafast time-resolved analytical methods for isotope ratio determination, identification and discrimination of close chemical species, and trace analysis.

Acknowledgement

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References

5.4 Selective control of molecular rotation (2008)

The article deals with our previous results on molecular spin isomers and molecular isotopologues. However the focus here is set to understanding and analyzing the frequency domains of the homodyne and heterodyne measurements, by comparing the frequency and time domains of the two. Data collected using the weak field polarization technique is presented with respect to the FWM scheme.
Selective control of molecular rotation

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Abstract

We demonstrate selective control over rotational motion of small, linear molecules. By means of sequential excitation of the rotational motion by ultrashort pulses, we first prepare transiently aligned molecules with periodically revived angular distribution. Upon further, properly timed excitation, the rotational energy can be increased or decreased, depending on the exact timing of the second pulse. We show how this approach can be applied for selective rotational control of a single component in a molecular mixture. We discuss this selectivity in the context of molecular isotopes ($^{14}N_2$, $^{15}N_2$), where the difference in isotopic mass gives rise to different rotational revival times. We further apply the method to the selective addressing of molecular spin isomers (para, ortho $^{15}N_2$) in a mixture, where wavefunction symmetry differences replace the mass differences as the origin of the selectivity. In both cases the method is demonstrated experimentally and the results are analysed theoretically.

(Some figures in this article are in colour only in the electronic version)

The interest in the field of laser alignment and orientation of molecules has been gradually increasing in the last few decades. The constantly improving ability to control the laser pulse characteristics (such as time duration and temporal shape) opened new possibilities for molecular rotational control. Since the typical rotational motion ($\sim 10$ ps) is ‘slow’ with respect to the typical short pulse ($\sim 50$ fs), effective rotational control and manipulation are in reach. In the liquid phase, molecular alignment following excitation by a strong laser pulse was observed in the 1970s [1], and proposed as a tool for optical gating. In the early experiments, picosecond laser pulses were used for the excitation, and deviation of the refractive index from that of an isotropic gas was monitored as evidence for alignment [2, 3]. More recently, these observations have been revisited both theoretically and experimentally (for a recent review, see [4]). Temporal rotational dynamics of pulse-excited molecules was studied [5–7], and multiple pulse sequences giving rise to the enhanced alignment were suggested [8, 9] and realized [10–13]. Further manipulations such as the optical molecular centrifuge and alignment-dependent strong field ionization of molecules were demonstrated [13–15]. Molecular phase modulators have been shown to compress ultrashort light pulses [16, 17] and molecular alignment has been used for controlling high harmonic generation [18–20]. Other experiments were reported where transient grating techniques were used for detailed studies of molecular alignment and deformation [21, 22].

In this work, we provide tools for coherent rotational excitation of a selected species in molecular mixtures (molecular isotopes [23] and mixtures of spin isomers [24]) as the first step towards the development of novel techniques for mixture analysis and separation.

Analysis and separation of molecular mixtures are two of the main goals of analytical chemistry and significant effort has been dedicated to the development of high-resolution analytical tools for these purposes. Most separation techniques are based on mechanical or electrical properties that the species to be separated differ by. As the molecular species to be separated become more similar in their properties, their analysis and separation becomes more demanding in the sense of the required resolution. In the extreme case, where no mechanical and electrical differences are to be found, the species in concern become hardly separable. In the case of molecular isotopes, separation methods which are based on the mass difference (such as centrifugation and gaseous diffusion) are known to be effective. In the case of molecular spin isomers, however, different nuclear spin modifications, such as ortho and para molecules, posses no mechanical or electrical differences, making them inseparable using the traditional analytic tools. We will address this problem in the part dealing with selective excitation of spin isomers.

Since our technique is based on transient molecular alignment, we start with a brief review of the basics of laser-induced molecular alignment.
1. Laser-induced molecular alignment

The physics of alignment of molecules by ultrashort laser pulses is well understood. A short non-resonant linearly polarized laser pulse induces a molecular dipole moment which in turn interacts with the electric field itself. Because of the generally anisotropic molecular polarizability, the laser field delivers a torque to the molecules, causing them to rotate towards the direction of the laser field polarization. A short time after the pulse (few hundreds of femtoseconds), the angular distribution of the molecules elongates along the direction of the field, and the molecular ensemble exhibits (partial) transient alignment under field-free conditions (see figure 1). The aligned angular distribution is symmetrical with respect to the direction of the field (‘up’ or ‘down’) and in what follows we refer to this geometrical shape as ‘cigar-like’, manifested in refractive index which is higher than the isotropic one. As time evolves, the molecules lose their alignment. Quantum mechanically, the laser pulse excites a wave packet which is formed from many rotational states, and which may be written as

\[ |\psi(\theta, t)\rangle = \sum_{J, m} c_{J, m} |J, m\rangle \exp(-iE_Jt) \]  

(1)

For linear molecules, the energy spectrum is given by \( E_J = \hbar Bc J(J + 1) \) (where \( B = \hbar / 4\pi Ic \) is the rotational constant, \( c \) is the speed of light and \( J \) is the molecular moment of inertia). According to equation (1), any such wave packet exactly reproduces itself at integer multiples of the revival time, \( T_{\text{rev}} = 1/(2Br) \). Moreover, as is well known [25], at rational fractions of the revival time \( T_{\text{rev}} \), fractional rotational revivals of the wave packet may also be observed. If it were possible to invert the direction of time, one would observe a strong anti-alignment (namely, a state where the molecules are in the plane perpendicular to the direction of alignment) just before the applied laser pulse. In this ‘anti-aligned’ state, the angular distribution geometry is of a ‘disk’ shape manifested in a lower refractive index. Remarkably, the effect of quantum revivals provides such an opportunity just before the revival time, because \( |\psi(\theta, T_{\text{rev}} - \tau)\rangle \approx |\psi(\theta, -\tau)\rangle \). Thus, every revived cigar-like angular distribution is preceded in time by a disk-like state. In addition, it can be shown [8] that the half-revival domain \( (\tau \approx T_{\text{rev}}/2) \) the aligned and anti-aligned states appear in the reversed order (see figure 1).

It is clear that ionization/dissociation of molecules by an additional laser pulse depends on the instantaneous angular distribution at the moment of the second pulse. Several authors demonstrated alignment-dependent strong field ionization of molecules [13, 26, 27]. In most cases, molecules tend to ionize and dissociate more easily by a field polarized along their maximal polarizability axis. The alignment of the molecules in the interaction region (even if transient) enables control over the ionization/dissociation rate. In particular, the ability to address a single aligned component in a mixture may lead the way to selectivity in ionization/dissociation, a step towards physical separation schemes.

2. Experimental details

We use a time-delayed degenerate, forward propagating, three-dimensional, phase-matched four-wave mixing arrangement [28], where the first two pulses set up a spatial grating of transiently aligned molecules, and the third delayed pulse is scattered off this grating. In our experiments, all three input beams (and therefore the fourth output beam as well) were linearly, vertically polarized. In this experimental arrangement, the contribution of the aligned and anti-aligned angular distributions to the signal is proportional to the square of the deviation of refractive index from the isotropic one, \( S \propto (\Delta n)^2 \). Because of the square dependence, only positive signals appear in figure 2(b) (to be discussed in details in section 2). The experiments were carried out at room temperature. The peak field intensity in the focal region was \( 3 \times 10^{13} \text{W cm}^{-2} \). Under these conditions, the rotational energy supplied to a nitrogen molecule by the laser pulse is comparable with (and even exceeds) the thermal rotational energy. Based on procedures described earlier [8, 29], we estimate the maximal degree of laser-induced alignment to be \( (\cos^2 \theta) \approx 0.5 \) (compared to the isotropic value of 0.33). The best antialignment is estimated to be of the order of \( (\cos^2 \theta) \approx 0.2 \). These estimations are consistent with the results of [11, 15], in which a comparable degree of \( N_2 \) alignment was directly measured (using Coulomb explosion imaging) under experimental conditions (pulse energy, duration and focusing) similar to ours.

3. Analysis of the FWM signals in the frequency domain

The quadratic dependence of the FWM signal on the induced variation of the refractive index, \( S \propto (\Delta n)^2 \), complicates the analysis of the alignment phenomenon. In what follows, we present the interpretation of the FWM signals in the frequency domain.
Figure 2. Comparison between alignment signals from weak-field polarization measurement (a) and degenerate four-wave mixing (b). The corresponding frequency domains are depicted in (c) and (d), respectively. The $J$ states in (c) and $J$ sums and differences are calculated from the actual frequencies and marked correspondingly.

Our measurements are performed in the time domain, where we scan the time delay between the first two pulses (applied simultaneously, serving as pump–dump) and the third (probe) pulse measuring the evolution of this coherence in time. If one measures the molecular alignment using a different method (known as ‘weak-field polarization technique’ [30]), in which $S \propto \Delta n$ (figure 2(a)), the frequency space reveals the fundamental $J$ states (figure 2(c)). However, the Fourier transform of the time domain FWM (figure 2(b)) signal reveals a more complex frequency pattern, demonstrating binary sums ($J + J'$) and differences ($J - J'$) of the fundamental $J$ states (marked in figure 2(d)).

The intensities of the even and odd binary sums (and differences) depend on the number of $J$ pairs contributing to each peak.

The difference of $J - J' = 1$ involves the maximal number of populated $J$ pairs, and should have yielded the most intense peak. However, as can be seen in figure 2(d), the most intense line is for $J - J' = 2$, and the reason lies in the even/odd population ratio. In the case of spin $\frac{1}{2}$, the even/odd ratio is 1:3. Therefore, the lines corresponding to even binary differences $J - J'$ (and sums $J + J'$) involve states of the same $J$ parity, resulting in peaks of higher intensity.

4. Control over the rotational motion

Following the application of a short, intense laser pulse, the molecules start to rotate giving rise to alignment, anti-alignment and other fractional revival signals due to the rotational wave packet evolution. In order to further manipulate molecular rotational motion, one needs to apply (at least) one more laser pulse. In a double pulse excitation scheme, the response of the molecular ensemble is very sensitive to the timing of the second pulse. If the second pulse is applied to a molecular ensemble evolving from disc to cigar states (near the time of full revival), its effect is similar to that of the first pulse, namely it kicks the molecules ‘in phase’ with their rotational motion, and adds angular momentum to the already rotating molecules. This results in a more pronounced alignment and in the increase of the rotational energy of the molecular wave packet. Quantum mechanically, the wave packet (equation (1)) at $\tau = T_{\text{rev}}$ is identical to the wave packet at $\tau = 0$; therefore, the molecules are affected by the two pulses delayed by full $T_{\text{rev}}$ in exactly the same way. This situation is illustrated by the measurements presented in figure 3(a). When the second pulse is applied exactly at $3T_{\text{rev}}$, the amplitude of the alignment peaks increases significantly.

If, on the other hand, the second pulse is applied when the molecular angular distribution evolves from cigar to disc (around the time of half revival), the torque impacted by the second pulse effectively cancels the coordinated motion of the rotating molecules, thwarting any future revivals. Quantum mechanically, the wave packet (equation (1)) at $\tau = \frac{1}{2}T_{\text{rev}}$ evolves ‘out of phase’ with respect to the initial wave packet at $\tau = 0$. This is well illustrated in figure 3(b), where the second pulse was applied at $2\frac{1}{2}T_{\text{rev}}$. These conclusions are also supported by other experiments in which molecular alignment was observed by weak-field polarization technique [31] and by Coulomb explosion imaging [32].
Let us note that this kind of control is most effective in the impulsive regime of excitation, in which the laser pulses are much shorter than the typical revival feature in the alignment dynamics. This imposes the following limitation on the pulse duration \( \tau_p \): \( \tau_p \ll \sqrt{I/(\Delta \alpha \varepsilon^2)} \). Here \( \Delta \alpha \) is polarizability anisotropy and \( \varepsilon \) is the amplitude of the pulse electric field. This requirement is well satisfied under the conditions of our experiments.

5. Selective rotational excitation of molecular isotopes

Gaseous diffusion and centrifugation are two examples for isotope separation techniques that rely on mechanical effects caused by small mass differences. Although these are rather general methods, they are relatively inefficient and require multiple separation stages. Laser isotope separation [33], on the other hand, provides high-single-stage enrichment, but it is molecule specific, and since done in the frequency domain, it necessitates tunable narrow-band laser sources. A promising separation methodology [34–37] based on laser-induced vibrational wave packets in excited electronic molecular states has been demonstrated, combining the advantages of the optical and mechanical methods, but it still relies on certain spectral selectivity.

In what follows, we consider non-resonant isotope-selective rotational control in a mixture of different molecular isotopes of the same chemical element, which potentially leads to new approaches to the analysis and separation of isotopic mixtures.

Following the application of an ultrashort laser pulse to a mixture of different molecules, a sequence of alignment and anti-alignment revivals is initiated. Since the species to be separated posses very close mechanical properties, their wave packets’ periodicities are almost the same. However, with time, different molecular ‘clocks’ become desynchronized due to the difference in the moments of inertia (and rotational constants), and at well-defined times, non-identical components (i.e. different isotopes) attain angular distributions which may be very different (i.e. cigar versus disc).

In section 2, we have shown that the application of the second pulse at full revival time results in enhancement of the coherent rotational motion whereas application at half-revival time, cancels the coherent excitation caused by the first pulse. The rational value of the isotopes mass ratio enables the addressing of the isotopic components by a second laser pulse such that one of them completes an integer number of revival times while the other completes an integer and a half of its own revival cycles.

In the case of a binary mixture of nitrogen isotopes \(^{15}\text{N}_2, \ ^{14}\text{N}_2\), the revival time \( T_{\text{rev}} \) equals to 8.9 ps and 8.3 ps, respectively. As a result, \(^{15}\text{N}_2\) completes \( 7 T_{\text{rev}} \) at ~63 ps after the first pulse, while \(^{14}\text{N}_2\) completes \( 7 \frac{1}{2} T_{\text{rev}} \). We apply the second laser pulse at this time and observe the enhancement of \(^{15}\text{N}_2\) alignment signals and the (almost) complete cancellation of the \(^{14}\text{N}_2\) ones (figure 4).

The exact overlap of the full and half revivals of \(^{15}\text{N}_2\) and \(^{14}\text{N}_2\), respectively, set the condition for their selective ionization/dissociation. Just before the exact overlap (63 ps), the \(^{15}\text{N}_2\) molecules attain a disk shape while the \(^{14}\text{N}_2\) ones are in cigar state. This unique situation makes \(^{14}\text{N}_2\) more suitable for ionization/dissociation by a strong pulse polarized in the direction of the cigar. Under the same laser conditions, the \(^{15}\text{N}_2\) molecules are less vulnerable. By adjusting the ionizing pulse intensity, one can selectively ionize/dissociate the \(^{14}\text{N}_2\) molecules without affecting the \(^{15}\text{N}_2\) ones. The opposite situation can be found just after 63 ps where the \(^{15}\text{N}_2\)
molecules attain a cigar shape while the \( ^{14}\text{N}_2 \) ones are in disk state.


In the case of molecular isotopes, we relied on small mass differences manifested in a slight mismatch of the revival times of the two molecular species. However, in the case of molecular spin isomers, their selective addressing becomes much more complicated since no mechanical or electrical differences are found. Specifically, similar mechanical properties of the spin isomers imply identical revival periodicity. A few practical applications of spin isomers are already known, motivating the search for novel separation techniques. Thus, spin isomers can affect chemical reactions \([38, 39]\), can significantly enhance NMR signals \([40, 41]\) or be used as spin labels in NMR-based techniques.

Linear symmetric molecules whose atomic constituents possess a nonzero nuclear spin exist as either ortho or para spin modifications, differing in the symmetry of their nuclear states. For a homonuclear diatomic molecule of spin \( \frac{1}{2} \) atoms, the total nuclear spin can be \( I = 1 \) (ortho molecule), or \( I = 0 \) (para molecule). This difference in symmetry implies statistical differences in the population of even and odd rotational states. Since spin changing radiative transitions are forbidden by symmetry, and spin changing collisions are very unlikely, these species are rather stable, and once prepared can be used and stored for long times. At low temperatures, ortho and para molecules can be, in principle, separated by cryogenic methods, but in practice, this has been applicable only for the lightest of all molecules, hydrogen.

Consider a spin \( \frac{1}{2} \) homonuclear diatomic molecule (e.g. \( ^{15}\text{N}_2, \text{H}_2 \)). Different spin quantum number combinations give rise to different symmetries of the rotational part of the wavefunction. For a spin \( \frac{1}{2} \) atom in a homonuclear diatomic, the spin symmetric molecular species (ortho) populate the odd rotational states and the antisymmetric ones (para) populate the even states. In the case of a spin 1 atom, the correlation between the symmetry and the rotational state parity is reversed due to the difference in the behaviour of fermions and bosons. The difference in the parity of rotational states populated by the different spin isomers provides a key for their selective manipulation and in fact, the problem of selective excitation of para or ortho isomers is reduced to selective excitation of even or odd rotational states.

In what follows, we consider the transient angular distribution of even (para) and odd (ortho) states following the application of a short laser pulse. Full quantum-mechanical simulation of nitrogen-like molecules at room temperature is depicted in figure 5, where even and odd states are shown separately. Around full and half-revival times (red background) the even and odd states behave similarly and at these times additional laser pulses will act on both species in a similar manner, precluding any selective control. However, around \( \frac{1}{4}T_{\text{rev}} \) and \( \frac{3}{4}T_{\text{rev}} \), the simulation reveals dramatic differences in the evolution of the alignment factor. This observation sets the stage for selective manipulation of the two isomers. For example, just before \( \frac{1}{4}T_{\text{rev}} \), the even states evolve from disc to cigar. At the same time, the odd states evolve in the reversed direction. The situation reverses just after \( \frac{3}{4}T_{\text{rev}} \). Using the same arguments as above, a pulse applied at these times affects the two species in the opposite ways, i.e. it increases the rotational energy of one of the species while reducing that of the other one.

Figure 6 depicts the calculated dependence of the rotational energy as a function of time delay between the first and second pulse. Around \( \frac{1}{4}T_{\text{rev}} \) and \( \frac{3}{4}T_{\text{rev}} \), the rotational energy content of the odd and even states can be manipulated such that an absorbed energy ratio of \( \sim 1/18 \) is within reach.
Figure 7. (a) Time domain FWM signal of $^{15}\text{N}_2$ at room temperature and the corresponding FFT (b). The second pulse is applied just before $1\frac{1}{4}T_{\text{rev}}$ in order to selectively excite the ortho isomers. The purity of excitation is manifested in the appearance of only even sums and differences of $J$ states (marked in (b)).

As an example, we consider the behaviour around a delay time slightly smaller than $\frac{1}{4}T_{\text{rev}}$. Here the ‘odd wave packet’ absorbs almost 20 times more rotational energy from the pair of pulses than the ‘even wave packet’. We note that the parameters used in this calculation were chosen to fit our experimental conditions (i.e. the pulse energy and sample temperature). Under these experimental conditions, the maximal energy supplied by the pulse to a molecule is $\sim 3$ times higher than the initial (thermal) rotational energy ($\sim 10^3$ in units of $\hbar Bc$, where $\hbar$ is Plank’s constant, $B$ is the $^{15}\text{N}_2$ rotational constant and $c$ is the speed of light). Thus, the pulse affects the molecules in a non-perturbative manner and introduces significant changes to the rotational wavefunction.

In the experiment we use the FWM setup described before, where we set two aligning pulses at some specific time delay and probe the wave packet evolution as a function of time. In the time domain we observe the alignment signals at all stages: the evolution following the first pulse and the evolution after the second pulse. As can be seen in figure 7(a), the first pulse (at $t = 0$) excites both para and ortho isomers, which is evidenced by the alternation of peak intensities due to the interference of the odd and even signals discussed above. The second pulse applied $\sim 150$ fs before $1\frac{1}{4}T_{\text{rev}}$ is followed by enhanced alignment signals of almost equal intensity. The reduction in the intensity alternation serves as an indication for the single spin isomer selective excitation since only molecules populating the same $J$ parity are excited. The purity of excitation is further verified in the frequency domain. Figure 7(b) depicts the Fourier transform of the signal following the second pulse. In the frequency domain, we observe only even sums and differences of the $J$ states. Since even binary sums and differences result from $J$ states of the same parity (even $= \pm$ even, odd $\pm$ odd) and odd binary sums and differences involve $J$ states of different parities (odd $= \pm$ odd), the complete removal of the odd $J$ sums and differences is a manifestation of the spin purity of excitation.

In order to determine the parity (and corresponding molecular species) of the $J$ states giving rise to the rotational coherence reflected by the alignment signals, we go back to the time domain in figure 7(a). As can be seen, the enhancement of the signal after the second pulse indicates that the ortho isomer was selectively addressed (odd $J$ states). Since the odd/even ratio is 3:1 in $^{15}\text{N}_2$ ($I = \frac{1}{2}$), only enhancement of the odd states and cancellation of the even ones will result in alignment signals of higher intensity. In the opposite case (not shown), the alignment signals are diminished by the second pulse.

The molecular response is very sensitive to the exact delay between the first and second pulses (‘evolution time’) as well as on the exact laser pulse parameters (intensity, duration). We analyse this response experimentally, by performing a two-dimensional scan where we probe the alignment signal along one full revival period for each ‘evolution time’ (figure 8).

Figure 8 shows the high-frequency domain of the double pulse FWM measurement. Each horizontal line depicts the $J + J'$ frequencies for specific evolution time (vertical axis) corresponding to delay of $\sim 1\frac{1}{4}T_{\text{rev}}$ for $^{14}\text{N}_2$. We identify two relevant time delays: 10.09 ps (dashed line) and 10.2 ps (solid line). Along these lines, only even sums of $J$ states are found, therefore corresponding to selective excitation of a molecular...
species populating a single $J$ parity. Since the nuclear spin of $^{14}\text{N}$ is $I = 1$ (boson), the correlation between the spin isomers and the $J$ state parity is different. In the case of $^{14}\text{N}_2$, the odd rotational states are populated by the para (antisymmetric spin function) isomers whereas ortho (symmetric spin function) ones populate the even rotational states. As the odd/even ratio is 1:2, judging by the relative intensities of the peaks along the dashed and dotted lines, we conclude that the dashed line corresponds to the selective excitation of the odd states (para isomers) and the solid line corresponds to the selective excitation of the even states (ortho isomers).

7. Summary

The application of a short laser pulse to gas phase molecular sample is followed by a series of aligned and anti-aligned molecular angular distributions. The repetitive character of these angular distributions was discussed both theoretically and experimentally. We have shown that by applying to the already rotating molecules another laser pulse at a proper time delay, we can enhance (or reduce) the coherent rotational motion in a nondestructive manner. Using these ‘rotational control tools’ we demonstrated the selective alignment of one molecular species in a mixture of nitrogen molecular isotopes ($^{14}\text{N}_2$, $^{15}\text{N}_2$), as the first step towards their physical separation by selective ionization/dissociation. Next we addressed nuclear spin isomers, and utilizing the known correlations between the spin and rotational wavefunctions and the different rotational behaviour of the even and odd rotational states, we demonstrated selective control over the rotation of para and ortho spin modifications. This method does not require resonant laser sources and is performed at room temperature. It is rather general and robust, and in principle, can be applied to all linear symmetric molecular species.

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5.5 Controlling the sense of rotation – (accepted by the New Journal of Physics, Sep 2009)
In this theoretical work, we explore the case of molecular interaction with two laser pulses having different polarizations for controlling the sense of molecular rotation. We calculate the angular momentum transferred to the molecular ensemble and analyze its evolution in time. The presented scheme opens several new directions in laser induced molecular rotation, as the ensemble presents an anisotropic angular distribution. We define a new observable – the azimuthal factor $\langle \cos^2 \varphi \rangle$ and calculate its time domain evolution. All calculations in this work are performed in two complementary ways (analytical by Sharly Fleischer and numerical by Yuri Khodorkovsky).
Controlling the sense of molecular rotation

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Abstract. We introduce a new scheme for controlling the sense of molecular rotation. By varying the polarization and the delay between two ultrashort laser pulses, we induce unidirectional molecular rotation, thereby forcing the molecules to rotate clockwise/counterclockwise under field-free conditions. We show that unidirectionally rotating molecules are confined to the plane defined by the two polarization vectors of the pulses, which leads to a permanent anisotropy in the molecular angular distribution. The latter may be useful for controlling collisional cross-sections and optical and kinetic processes in molecular gases. We discuss the application of this control scheme to individual components within a molecular mixture in a selective manner.

The essence of coherent control is to drive a molecular system towards specific behavioural goal. The goals are usually set as the enhanced population of a specific vibrational or electronic state and the tools are ultrashort laser pulses, which are modulated either in the time or frequency domains. Here, we present a double-pulse scheme for controlling the sense (clockwise/counterclockwise) of the molecular rotation.

Laser-induced molecular rotation and alignment has received significant attention in recent years. In the last decade, interest in the field has increased, mainly due to the improving capabilities to control the laser pulse characteristics (such as time duration and temporal shape), which in turn leads to potential applications offered by controlling the angular distribution of molecules. Since the typical rotational motion is ‘slow’ (~10 ps) with respect to the typical short pulse (~50 fs), effective rotational control and manipulation are in reach. In the liquid phase, molecular alignment following excitation by a strong laser pulse was observed in the

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seventies [1], and proposed as a tool for optical gating. In the early experiments, picosecond laser pulses were used for the excitation, and deviation of the refractive index from that of an isotropic gas was utilized as a measure of the alignment [2, 3]. More recently, this research area has been revisited both theoretically and experimentally\(^3\). Temporal rotational dynamics of pulse-excited molecules was studied [5]–[7], and multiple pulse sequences giving rise to the enhanced alignment were suggested [8, 9], and realized [10]–[13]. Further manipulations such as optical molecular centrifuge and alignment-dependent strong field ionization of molecules were demonstrated [13]–[15]. Selective rotational excitation in bimolecular mixtures was suggested and demonstrated in the mixtures of molecular isotopes [16] and spin isomers [17]. Transient molecular alignment has been shown to compress ultrashort light pulses [18, 19] and it is successfully used in controlling high harmonic generation [20]–[22]. Other experiments were reported in which transient grating techniques were employed for detailed studies of molecular alignment and deformation [23, 24]. In the past few years, molecular alignment became a common tool in attosecond studies, in particular, in experiments for probing molecular bond structures [25, 26].

In practically all the previous works in the field of laser molecular alignment (with the exception of [14]), the rotational motion was enhanced, but the net total angular momentum delivered to the molecules remained zero, and for a good reason. For single-pulse schemes, as well as for techniques using multiple pulses polarized in the same direction, no preferred sense of rotation exists due to the axial symmetry of excitation.

In order to inject angular momentum to the medium and to force the molecules to rotate with a preferred sense of rotation, one has to break the axial symmetry. This has been previously demonstrated by Karczmarek et al [14] who used two oppositely chirped, circularly polarized pulses overlapping in time and space, thereby creating a linearly polarized pulse, rotating unidirectionally and accelerating in a plane.

In solid state, controlled unidirectional rotation of induced polarization by impulsive excitation of twofold degenerate lattice vibrations was demonstrated in \(\alpha\)-quartz [27].

In this paper, we propose a double-pulse scheme for breaking the axial symmetry and for inducing unidirectional molecular rotation under field-free conditions.

Pictorially, our double-pulse control scheme is sketched in figure 1. An ultrashort laser pulse (red arrow), linearly polarized along the \(z\)-axis, is applied to the molecular ensemble and induces coherent molecular rotation. The molecules rotate under field-free conditions until they reach an aligned state, in which they are temporarily confined in a narrow cone around the polarization direction of the first pulse. At this moment, a second pulse, linearly polarized at 45° to the first one, is applied, inducing unidirectional (clockwise, in our case) molecular rotation.

In the present paper, we discuss the dependence of the induced angular momentum on the pulse intensities, and the delay between pulses. Moreover, we focus on the molecular angular distribution when the molecules are subject to unidirectional rotation, and show that it is confined in the plane defined by the two polarization vectors of the pulses. This anisotropic angular distribution is characterized by the observable \(\langle \cos^2 \phi \rangle\) which is referred to as the azimuthal factor. This highly anisotropic angular distribution induced by the breaking of the axial symmetry may offer an efficient way to control the kinetic and optical properties of the gas medium.

\(^3\) For recent review on laser-induced alignment, see [4].
We consider the problem by modelling the molecules as driven rigid rotors interacting with a linearly polarized laser field. Within this model the Hamiltonian of the linear molecules is given by

\[ H = \frac{\hat{J}^2}{2I} + V(\theta, t), \]  

where \( \hat{J} \) is the angular momentum operator, \( \theta \) is the angle between the polarization vector of the field (defining the \( z \)-axis) and the molecular axis, and \( I \) is the moment of inertia of the molecule. The latter is related to the molecular rotational constant \( I = \hbar / (4\pi cB) \), where \( \hbar \) is the Planck constant and \( c \) is the speed of light. The interaction term is given by

\[ V(\theta, t) = -\frac{1}{4} \varepsilon^2(t) [(\alpha_|| - \alpha_\perp) \cos^2(\theta) + \alpha_\perp], \]

where \( \varepsilon(t) \) is the envelope amplitude of the laser field, and \( \alpha_||, \alpha_\perp \) are the parallel and perpendicular components of the polarizability tensor, respectively.

We simulated the proposed scheme quantum-mechanically by two independent methods. The first of them is mainly analytical: it uses spectral decomposition of the time-dependent rotational wavefunction, and relies heavily on angular momentum algebra for calculating the observable quantities (see appendix A for the mathematical details). Such an approach has been widely used in the past by many groups, including ourselves [8, 9], to analyse multipulse alignment. The second method uses direct numerical simulation of the driven ensemble of quantum rotors by means of finite-difference time-domain (FDTD) approach (for details, see appendix B). In both cases, the laser pulses were approximated as \( \delta \) functions, and their integrated ‘strength’ was characterized by a dimensionless pulse strength parameter

\[ P = (\Delta \alpha / 4\hbar) \int_{-\infty}^{+\infty} \varepsilon^2(t) \, dt, \]

where \( \Delta \alpha = \alpha_|| - \alpha_\perp \). Physically, the parameter \( P \) represents a typical increase of the molecular angular momentum (in the units of \( \hbar \)) due to the interaction with the pulse. All simulations were performed at finite temperature, and the results were averaged over a thermal molecular ensemble. Moreover, recently the same problem was studied by us classically with the help of the Monte Carlo method, the details are given elsewhere [28]. All three approaches gave qualitatively similar outcome, with two quantum treatments (presented here) yielding essentially identical results. For the sake of brevity, in the body of the paper we present the results of the
Figure 2. Expectation value of the angular momentum along the y-axis as a function of the polarization angle of the second pulse. The pulse intensities are given by $P_1 = 3$ and $P_2 = 6$ (see text for definitions), the temperature is 100 K (for Nitrogen molecules). The second pulse is applied at the maximally aligned state, just before $1/2T_{rev}$. The direction of the molecular rotation is depicted by the cartoons, showing clockwise and counterclockwise rotation for $45^\circ$ and $-45^\circ$, respectively.

quantum calculations briefly, and the readers are referred to appendices A and B where the details of calculations are given.

We consider separately the evolution of molecules starting from individual eigenstates of the rigid rotor (described by a spherical harmonic $Y_{lm}^m(\theta, \phi)$). The action of the first laser pulse (polarized in the z-direction) was approximated by impulsive excitation and then the resulting wavepacket was propagated in time using either the spectral decomposition of the wavefunction

$$\psi(\theta, \phi, t) = \sum_l C_{l,m} e^{-iE_l t/\hbar} Y_{l}^{m}(\theta, \phi)$$

(here $E_l$ is the energy of the lth eigenstate of the rigid rotor), or by means of direct FDTD simulation. Next, we calculated the thermally averaged alignment factor $\langle \cos^2 \theta \rangle$ and found the time of maximal alignment, just before $1/2T_{rev}$ (see inset to figure 2). Here $T_{rev} = 1/(2Bc)$ is the rotational revival time. At this time, we applied the second $\delta$-pulse, linearly polarized in the $xz$-plane at an angle $\theta_p$ with respect to the vertical $z$-direction. The second pulse creates much richer wavepackets that are composed of states having different $m$ quantum numbers. By using the spectral decomposition again (appendix A), or FDTD simulation (appendix B) we calculated the angular momentum and the time-dependent azimuthal factor $\langle \cos^2 \phi \rangle$ after the second pulse. Finally, the results were thermally averaged by repeating the calculation for different initial states $Y_{l}^{m}(\theta, \phi)$, and adding them with proper statistical weights.

In figure 2, we present the calculated expectation value of the y-component of the angular momentum ($\langle J_y \rangle$) as a function of the polarization angle of the second pulse. The second pulse
Figure 3. Maximal alignment factor of the aligned state, just before $1/2T_{\text{rev}}$ for different pulse strength ($P_1$) at 150 K (for nitrogen molecules). The dependence is fairly linear in the shown parameter region. At higher pulse power, the alignment factor saturates at $\sim 0.9$.

is applied at the time of maximal alignment (marked by an arrow in the inset) just before the one-half rotational revival following the first aligning pulse.

The maximal angular momentum is achieved when the second pulse is polarized at $\pm 45^\circ$ with respect to the first pulse polarization. This result is in agreement with the classical description of the light–rotor interaction. The interaction term in the Hamiltonian is given by $V = -\frac{1}{4} \varepsilon \Delta \alpha \cos^2 \theta$, therefore the torque applied to a molecule oriented at angle $\theta$ to the pulse polarization is given by $\tau(\theta) \propto -\frac{dV}{d\theta}$, and the corresponding angular velocity gained by the molecule is $\omega(\theta) \propto -\sin(2\theta)$. Thus, the maximal velocity is gained by a molecule initially aligned at $\theta = \pm 45^\circ$ to the field.

As the next step we explore the dependence of the induced angular momentum on the strength $P_{1,2}$ of the two laser pulses. Figure 3 shows $\langle \cos^2 \theta \rangle$ of the aligned state just before $1/2T_{\text{rev}}$ as a function of the first pulse strength $P_1$.

Figure 4 shows the angular momentum induced by the double-pulse excitation. We scan the power of the second pulse ($P_2$) for each of the $P_1$ values shown in figure 3.

As $P_1$ and $P_2$ increase, so does the induced angular momentum. Looking at the line slopes in figure 4, one can immediately deduce a clear trend: as the power of the first pulse increases, so does the slope, i.e. the ability of inducing angular momentum by the second pulse increases with the first pulse power (and the corresponding alignment factor). If the total energy of two laser pulses is fixed ($P_1 + P_2 = P_{\text{tot}}$), one may ask what is the best pair of pulses leading to the maximal induced angular momentum. Figure 5 depicts $\langle J_y \rangle$ as a function of $P_1 - P_2$ for $P_{\text{tot}} = 13$ (for rotational temperature of 150 K in the case of nitrogen).

Figure 5 shows quadratic dependence of $\langle J_y \rangle$ on $P_1 - P_2$, for a fixed pulse power $P_{\text{tot}}$. The maximal angular momentum is found for $P_1 = P_2 = P_{\text{tot}}/2$. This result is in agreement with the linear character of the plots shown at figures 3 and 4.

Up to now, we have shown that if the second pulse is applied at the time of maximal molecular alignment caused by the first pulse (see inset of figure 2), then the maximal
Figure 4. Induced angular momentum as a function of the strength of the second pulse, $P_2$ calculated for different strength $P_1$ of the first pulse at 150 K (for nitrogen molecules).

Figure 5. Calculation of the induced angular momentum $\langle J_y \rangle$ as a function of $P_1 - P_2$. The total strength of the two pulses was kept constant $P_{\text{tot}} = P_1 + P_2 = 13$, at 150 K (for nitrogen molecules).

unidirectionality is achieved when the second pulse is polarized 45° to the first one. In what follows, we keep the polarization at 45° and vary the delay between the two laser pulses.

Figure 6 shows the induced angular momentum $\langle J_y \rangle$ for the fixed pulse strengths $P_1$ and $P_2$ as a function of the time delay between the two pulses around $1/2T_{\text{rev}}$.

If the second pulse is applied just before the $1/2T_{\text{rev}}$, when the molecular distribution peaks in the $z$-direction, the clockwise unidirectional rotation is induced in the molecular medium. But if the second pulse is applied just after $1/2T_{\text{rev}}$, when the molecules are anti-aligned, the
unidirectional rotation is counterclockwise. For nitrogen molecules, the difference between these two time delays is about 200 fs.

In a mixture of two species such as molecular isotopes [16], one can find time delays when one species is aligned while the other is anti-aligned at the same time. Application of the second pulse at this time moment will result in the opposite senses of rotation induced for the two species, which can be potentially used for their physical separation.

In figure 7, we show a calculation similar to the one in figure 6 but now we scan the time delay between the two pulses around $1/2T_{\text{rev}}$. As we showed recently [17], different spin isomers of homonuclear diatomic molecules experience opposite alignment dynamics in this region. When the second pulse is applied exactly at $1/4T_{\text{rev}}$, para and orthonuclear spin isomers acquire opposite senses of rotation. The reason for this phenomenon is the drastically different angular distributions (alignment versus anti-alignment) that the para and the orthomolecules attain in this time domain [17].

Finally, we concentrate on the angular distribution of molecules excited by our double-pulse scheme. Classically, we expect that unidirectionally rotating molecules remain confined to the plane defined by the two polarization vectors of the pulses. To investigate this problem in detail, we consider a new observable $\langle \cos^2 \phi \rangle$ correlated with molecular confinement to this plane (where $\phi$ is the azimuthal angle). In figure 8, we plot $\langle \cos^2 \phi \rangle$ as a function of time. We start from the point where the second pulse is applied, since before that $\langle \cos^2 \phi \rangle = 1/2$, and it is time independent.

One can clearly observe the features of the revival phenomenon manifested in the peaks (dips) of $\langle \cos^2 \phi \rangle$ at different fractional times within one revival period. Note that in contrast to the alignment factor $\langle \cos^2 \theta \rangle$, showing only full, half and quarter revivals, the azimuthal factor $\langle \cos^2 \phi \rangle$ clearly exhibits higher fractional revivals.

At higher temperatures and higher excitation powers, the fractional revivals are better observed. In figure 9, we plot $\langle \cos^2 \phi \rangle$ as a function of time for $P_1 = P_2 = 10$ at 150 K for nitrogen molecules.
Figure 7. Calculation of the induced angular momentum $\langle J_y \rangle$ as a function of time delay between the pulses around $1/4T_{\text{rev}}$. $P_1 = 3$, $P_2 = 6$ and the temperature is $100\, \text{K}$ (for nitrogen molecules).

Figure 8. $\langle \cos^2 \varphi \rangle$ as a function of time after the second pulse calculated by the analytical method (dashed black line), and FTDT approach (solid red line). $P_1 = P_2 = 5$, for nitrogen molecules at temperature of $50\, \text{K}$.

Note that fractional revivals around $1/3$, $1/6$, $1/8T_{\text{rev}}$ of the revival are clearly observed. Furthermore, the time-average value of $\langle \cos^2 \varphi \rangle$ in figure 9 is $\sim 0.57$, which certainly exceeds the isotropic value of 0.5. This means that the molecular axis indeed preferentially occupies the plane defined by the two polarization directions. For details of the calculation of $\langle \cos^2 \varphi \rangle$ we refer the reader to appendices A and B.

Figure 10 depicts the angular distribution (averaged over one full revival period) after the second pulse, confirming the confinement of the molecules to the plane.
Figure 9. $\langle \cos^2 \varphi \rangle$ as a function of time after the second pulse. $P_1 = P_2 = 10$ and the temperature is 150 K (nitrogen molecules).

Figure 10. Angular distribution of the unidirectionally rotating molecules averaged over one full revival shown from two perpendicular view directions.

The induced anisotropy leads to anisotropic cross-sections for collisions of the molecules between themselves, or with atoms/molecules of a buffer gas. This may result in controlled anisotropic diffusion of different species in a molecular mixture. Moreover, the persistent anisotropy allows for controlling the gas-surface scattering phenomena. These and other related problems are a subject of an ongoing research.

Summarizing, we have shown that by applying two non-parallel-polarized ultrashort laser pulses one can break the axial symmetry of molecular rotation and control the sense of the rotation, thereby injecting angular momentum to the molecular ensemble. The sense of rotation depends on the relative timing and angle between the polarization directions of the pulses. This double-excitation scheme can be used for selective-excitation of unidirectional rotation in mixtures of molecular isotopes and spin isomers. An important outcome is the anisotropic confinement of the molecules to the plane defined by the two polarizations, which leads to anisotropic collisional cross-sections, which may offer a novel way for controlling kinetic processes in molecular gases.
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Appendix A. Double-pulse scheme: analytical treatment

We consider the action of the laser pulses in the impulsive approximation (i.e. assuming that they are much shorter than the typical timescales of the rotational motion) by treating them as δ-pulses. During the δ-pulse, one may neglect the kinetic energy term in the Schrödinger equation, which can be solved exactly after that. As the result, the rotational wavefunction just after the pulse, \( \psi^+ \), is related to the wavefunction \( \psi^- \) just before the pulse by

\[
\psi^+ = \exp[iP \cos^2 \theta] \psi^-.
\]

Here, \( P = (\Delta \alpha / 4\hbar) \int_{-\infty}^{+\infty} \epsilon^2(t) \, dt \) is the dimensionless strength of the pulse. In this calculation, the initial states \( \psi^- \) are the eigenstates \( Y^m_\theta(\theta, \phi) \) of the rigid rotor. To consider the post-pulse evolution, we decompose the resulting \( \psi^+ \) in the basis of spherical harmonics. Despite the simple look of the impulsive transformation, this decomposition is a nontrivial task that can be done by several methods (see, e.g. [8, 29]). In our case, we introduce the artificial ‘time’-parameter \( \tau \), and consider the \( \tau \)-dependent construction

\[
e^{iP \cos^2 \theta \tau} \psi^- = \sum_{l,m} C_{l,m}(\tau) Y^m_l(\theta, \phi).
\]

We convert the problem to the solution of a set of coupled differential equations for the coefficients \( C_{l,m}(\tau) \). At \( \tau = 0 \) only the coefficient corresponding to the initial eigenstate is nonzero (and equal to 1). The after-pulse wavefunction \( \psi^+ \) is given by (6) at \( \tau = 1 \). The needed set of differential equations is produced by differentiating (6) with respect to \( \tau \), and projecting both sides of the resulting equation to \( \langle Y^{m'}_l | \cos^2 \theta | Y^m_l \rangle \):

\[
\hat{\mathbf{C}}_{l',m'}(\tau) = iP \sum_{l,m} C_{l,m}(\tau) \langle Y^{m'}_l | \cos^2 \theta | Y^m_l \rangle.
\]

We write \( \cos^2 \theta \) in terms of the spherical harmonic functions:

\[
Y^0_2(\theta, \phi) = \frac{1}{4\sqrt{\pi}} (3 \cos^2 \theta - 1) \Rightarrow \cos^2 \theta = \frac{4}{3} \sqrt{\frac{\pi}{5}} Y^0_2(\theta, \phi) + \frac{1}{3}.
\]

For the integration of the product of three spherical harmonic functions, we use the Wigner 3j symbol:

\[
\int_0^{2\pi} \int_0^\pi Y^m_{l_1} Y^m_{l_2} Y^m_{l_3} \sin \theta \, d\theta \, d\phi = \sqrt{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)} \frac{4\pi}{4\pi} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.
\]
Equations (7) become
\[ \dot{C}_{l,m}(\tau) = iP \frac{4}{3} \sqrt{\frac{\pi}{3}} \sum_{l,m} C_{l,m}(\tau) \langle Y^m | Y_0 | Y^m \rangle + \frac{iP}{3} C_{l,m}(\tau). \] (9)

From the equations above, one can see that the interaction term \(\propto \cos^2 \theta\) couples the \(|l, m\rangle\) states only to the \(|l \pm 2, m\rangle\) states. Thus the resulting wavepacket consists of states having the same parity (odd/even) as the initial state, and with the same \(m\) number.

After decomposing \(\psi^{(+)}\) in the form of (6) (with \(\tau = 1\)), we propagate this wavepacket in time for every possible initial state, and calculate the thermally averaged alignment factor \(\langle \cos^2 \theta \rangle\) as a function of time. At the moment of the maximal alignment, just before \(1/2T_{rev}\), we apply the second pulse, polarized in the \(xz\)-plane at an angle \(\theta_p\) with respect to the \(z\)-axis.

The interaction with the second pulse is proportional to \(\cos^2 \beta\), where \(\beta\) is the angle between the molecular axis and the inclined polarization vector:
\[ \cos^2 \beta = \cos^2 \varphi \sin^2 \theta \sin^2 \theta_p + \cos^2 \varphi \cos^2 \theta_p + \cos \varphi \sin \theta \cos \theta \sin(2\theta_p). \] (10)

After some algebra we express the angular-dependent functions in (10) as
\[ \cos^2 \varphi \sin^2 \theta = \sqrt{\frac{\pi}{15}} (Y_2^2 + Y_{-2}^2) - \frac{2}{3} \sqrt{\frac{\pi}{5}} Y_2^0 + \frac{1}{3}, \]
\[ \cos^2 \theta = \frac{4}{3} \sqrt{\frac{\pi}{3}} Y_2^0 + \frac{1}{3}, \]
\[ \cos \varphi \sin \theta \cos \theta = \sqrt{\frac{2\pi}{15}} (Y_2^{-1} - Y_2^1). \]

To consider the action of the second pulse in the impulsive approximation (similar to (6) and (7)) we have to solve the following set of coupled differential equations:
\[ \dot{C}_{l,m}(\tau) = iP \sum_{l,m} C_{l,m}(\tau) \left\{ \sin^2 \theta_p \left[ \sqrt{\frac{\pi}{15}} \langle Y^m | Y_2^{-2} | Y^m \rangle + \sqrt{\frac{\pi}{15}} \langle Y^m | Y_2^2 | Y^m \rangle \right] + \frac{1}{3} \langle Y^m | Y_2^0 | Y^m \rangle - \frac{2}{3} \sqrt{\frac{\pi}{5}} \langle Y^m | Y_0^0 | Y^m \rangle \right\} + \cos^2 \theta_p \left[ \frac{4}{3} \sqrt{\frac{\pi}{5}} \langle Y^m | Y_2^0 | Y^m \rangle + \frac{1}{3} \langle Y^m | Y_0^m \rangle \right] + \sin(2\theta_p) \left[ \sqrt{\frac{2\pi}{15}} \langle Y^m | Y_2^{-1} | Y^m \rangle - \sqrt{\frac{2\pi}{15}} \langle Y^m | Y_2^1 | Y^m \rangle \right]. \]

In contrast to the case of the first pulse, different \(m\)-states are now coupled to states with \(m \pm 1\) and \(m \pm 2\), thus leading to the generation of more complex angular wavepackets. By solving the above equations on the interval \(0 \leq \tau \leq 1\), one is able to decompose the resulting wavepackets in the basis of rotor eigenstates, and to define their time-dependent dynamics.

As mentioned in the main text, the induced unidirectional rotation is accompanied by the confinement of the molecular angular distribution to the plane defined by polarization vectors of the two pulses. We introduce an observable \(\langle \cos^2 \varphi \rangle\) (where \(\varphi\) is the azimuthal angle) correlated with molecular confinement to the plane. One may present the quantum-mechanical average as \(\langle \psi | \cos^2 \varphi | \psi \rangle = 1/2 + 1/4 \langle \psi | e^{i2\varphi} | \psi \rangle + c.c.\) Using the expansion of the wavefunction \(\psi\) in spherical harmonics \(\psi = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_{l,m} Y_l^m\) and the explicit expression for \(Y_l^m\)
\[ Y_l^m(\theta, \varphi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi (l+m)!}} P_l^m(\cos \theta) e^{im\varphi} \] (12)

(where \( P_l^m(\cos \theta) \) is the associated Legendre polynomial), one arrives at

\[
\langle \psi | e^{i2\varphi} | \psi \rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{l} \sum_{m'=-l'}^{l'} C_{l,m}^* C_{l',m'} \left\{ Y_l^m | e^{i2\varphi} | Y_{l'}^{m'} \right\}
\]

\[
= \frac{1}{2} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{l} \sum_{m'=-l'}^{l'} C_{l,m}^* C_{l,m-2} \sqrt{(2l+1)(2l'+1)(l-m)!(l-m+2)!}
\]

\[
(1+m)!(1+m-2)!
\]

\[
\times \int_0^\pi P_l^m(\cos \theta) P_{l'}^{m-2}(\cos \theta) \sin \theta d\theta.
\]

(13)

Here, we used the fact that \( e^{i2\varphi} \) couples only \( m \) and \( m-2 \) eigenstates.

For the overlap integral of associated Legendre polynomials in (13), we used Wong’s formula [30]:

\[
\int_0^\pi P_{l_1}^{m_1}(\cos \theta) P_{l_2}^{m_2}(\cos \theta) \sin \theta d\theta = \sum_{p_1=0}^{p_{1\text{max}}} \sum_{p_2=0}^{p_{2\text{max}}} a_{l_1,m_1}^{p_1} a_{l_2,m_2}^{p_2}
\]

\[
\times \frac{\Gamma\left(1/2(l_1+l_2-m_1-2p_1-2p_2+1)\right) \Gamma\left(1/2(m_1+m_2+2p_1+2p_2+2)\right)}{\Gamma\left(1/2(l_1+l_2+3)\right)},
\]

(14)

where

\[
da_{l,m}^p = \frac{(-1)^p (l+m)!}{2^{m+2p} (m+p)! (l-m-2p)!
\]

\[
p_{\text{max}} = [(l-m)/2], \quad \text{which is the integer part of } (l-m)/2,
\]

(15)

\[
l = 0, 1, 2, \ldots \quad \text{and} \quad 0 \leq m \leq l.
\]

In order to calculate the overlap integral for negative \( m \)’s, we used the formula:

\[
P_l^{-m}(\cos \theta) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta).
\]

(16)

The time-dependent thermally averaged value of the azimuthal confinement factor \( \langle \cos^2 \varphi \rangle \) calculated by this technique is presented in figure 8.

**Appendix B. Double-pulse scheme: FDTD simulation**

In order to avoid algebraic complications in treating the double-pulse scheme in the basis of free rotor eigenstates, we undertook a direct numerical solution of the problem by FDTD method. After introducing the dimensionless time, \( \tau = (h/1)t \) (where \( I \) is the moment of inertia of the molecule), the time-dependent Schrödinger equation takes the following form:

\[
\frac{i}{\partial \tau} \psi = \frac{1}{2} \hat{\sigma}_2 \psi + v(\theta, \varphi, \tau) \psi.
\]

(17)
The angular momentum operator squared is given by
\[
\hat{\ell}^2 = -\left( \frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right).
\] (18)

The dimensionless interaction potential describing the interaction of the pulse with the induced polarization is
\[
v(\theta, \phi, \tau) = -\frac{I}{4\hbar^2} \varepsilon^2(\tau) \Delta \alpha \cos^2 \beta
\] (19)

Compared to (2), we consider pulse polarization vector pointing in an arbitrary direction, and \( \beta = \beta(\theta, \phi) \) is the angle between the molecule axis and this vector. In addition, we omitted the insignificant angle-independent term in (2). For our specific problem, the effect of each of the two laser pulses on the wavefunction was considered in impulsive approximation (5)
\[
\psi^{(+)} = \exp \{iP \cos^2 \beta\} \psi^{(-)},
\] (20)

where the pulse strength, \( P \) is defined in (3). The system evolution between the pulses (and after them) is governed by the free Hamiltonian that is azimutally symmetric. This allows us to reduce the two-dimensional time-dependent problem to a set of one-dimensional ones by performing the Fourier transformation in the azimuthal variable \( \varphi \):
\[
\psi(\theta, \varphi, \tau) = \sum_{m=-\infty}^{\infty} f_m(\theta, \tau) \exp(i m \varphi),
\] (21)

where
\[
f_m(\theta, \tau) = \int_{0}^{2\pi} \psi(\theta, \varphi, \tau) \exp(-i m \varphi) \, d\varphi.
\] (22)

From the Schrödinger equation, we obtain an infinite set of equations:
\[
\frac{\partial f_m}{\partial \tau} = \frac{i}{2} \left( \frac{\partial^2 f_m}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial f_m}{\partial \theta} - \frac{m^2 f_m}{\sin^2 \theta} \right), \quad m = 0, \pm 1, \pm 2, \ldots
\] (23)

Note that there are cases when only one equation of the set (23) has to be solved. This is, for example, the case when one of the eigenstates of the free rotor, \( Y_l^m(\theta, \phi) \) is kicked by a pulse polarized along the \( z \)-axis. In this case, \( \beta \) in (20) coincides with the polar angle \( \theta \), and the wavefunction just after the pulse becomes
\[
\psi^+(\theta, \phi) = \exp(iP \cos^2 \beta) \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos \theta) e^{im\varphi}
\] (\( P_l^m \) is the associated Legendre polynomial.

In the general case, we use the fast Fourier transform (FFT) algorithm to calculate \( f_m(\theta, \tau = 0) \).

In order to solve the set of equations (23) numerically, one needs to discretize it on a \( \theta \)-grid. A natural choice for the grid points is \([0, \delta \theta, 2\delta \theta, \ldots, \pi]\) (here \( \delta \theta \) is the grid step), but then one faces singularities in the coefficients of equations (23) at the north pole, \( \theta = 0 \), and at the south pole, \( \theta = \pi \). There are several ways of dealing with this problem, such as imposing the pole conditions \([31, 32]\), or using Fourier decomposition \([33]\). We choose another method \([34]\),
because of its simplicity. We shift the grid by half a distance between adjacent grid points, to avoid placing points at the poles: \([ \delta \theta / 2, 3 \delta \theta / 2, \ldots, \pi - \delta \theta / 2 ]\). Discretizing equation (23) and using the central-difference approximation for the first derivative, we obtain

\[
\frac{d f^i_m}{d \tau} = \frac{i}{2} \left( \frac{f^{i-1}_m - 2f^i_m + f^{i+1}_m}{\delta \theta^2} + \frac{f^{i+1}_m - f^{i-1}_m}{2\delta \theta \tan \theta_i} - \frac{m^2 f^i_m}{\sin^2 \theta_i} \right),
\]

(25)

where the superscript \(i\) numerates the points on the grid. For the end-points of the grid, the values of the function \(f_m(\theta)\) at ‘non-physical’ arguments \(-\delta \theta / 2\) and \(\pi + \delta \theta / 2\) are needed to calculate the derivatives. Using the symmetry of the wavefunction in spherical coordinates \(\psi(-\theta, \varphi) = \psi(\theta, \varphi + \pi), \psi(\pi + \theta, \varphi) = \psi(\pi - \theta, \varphi + \pi)\),

we obtain the following boundary conditions for \(f_m(\theta, \tau)\) at these ‘non-physical’ points:

\[
f_m(-\delta \theta / 2) = (-1)^m f_m(\delta \theta / 2); \quad f_m(\pi + \delta \theta / 2) = (-1)^m f_m(\pi - \delta \theta / 2)
\]

(27)

To propagate the wavefunction in time, we used the Crank-Nicolson method [35]

\[
f_m(\tau + \delta \tau) = U f_m(\tau) = \frac{1 - iH\delta \tau / 2}{1 + iH\delta \tau / 2} f_m(\tau),
\]

(28)

which is second-order accurate in \(\delta \tau\), and is explicitly unitary \((U^\dagger = U^{-1})\). Here matrix \(H\) presents the discretized Hamiltonian corresponding to the set of equations (25). In order to avoid heavy matrix inversion and multiplication, we rewrite (28) as:

\[
f_m(\tau + \delta \tau) = \left( \frac{2}{1 + iH\delta \tau / 2} - 1 \right) f_m(\tau) = 2\chi(\tau) - f_m(\tau),
\]

(29)

where \(\chi(\tau)\) is the solution of a tridiagonal linear system

\[
(1 + iH\delta \tau / 2) \chi(\tau) = f_m(\tau).
\]

(30)

Solving the tridiagonal system (30) by backward/forward sweep method is much more efficient numerically than a direct implementation of equation (28).

After calculating numerically \(f_m(\theta, \tau)\) for all \(m\), we use (21) to determine the time-dependent wavefunction \(\psi(\theta, \varphi, \tau)\).

For a finite temperature system, this procedure was repeated for all relevant initial \(|\ell, m\rangle\) states (which are populated according to the thermal distribution) and the corresponding wavefuctions \(\psi^{lm}_{\ell, m}(\theta, \varphi, \tau)\) were defined. The population of the initial \(|\ell, m\rangle\) state is given by \(W_{\ell m} = \exp (-E_{\ell} / kT) / Z\), where \(E_{\ell} = hB(\ell + 1)\) is the energy of the rigid rotor eigenstate, \(B\) is the rotational constant, \(Z\) is the partition function, \(T\) is the temperature and \(k\) is the Boltzmann constant. The time dynamics of the average value of any observable \(\hat{B}\) depending on \(\theta\) and \(\varphi\), may be calculated according to

\[
\langle \hat{B} \rangle(\tau) = \int_0^{2\pi} \int_0^\pi \left( \sum_{\ell, m} W_{\ell m} |\psi^{\ell m}_{\ell, m}(\theta, \varphi, \tau)|^2 \right) B(\theta, \varphi) \sin \theta \, d\theta \, d\varphi.
\]

(31)

In particular, we used this procedure, to calculate the time-dependent azimutal factor \(\langle \cos^2 \varphi \rangle\) shown in figure 8.
References

[31] Khodorkovsky Y and Averbukh I Sh (to be published)
[34] Yee S Y K 1981 Mon. Weather Rev. 109 501

6. Supplementary material (unpublished)

In section 5.3 (article named: Spinning molecules selectively: laser control of isotopes and nuclear spin isomers) we presented the FWM signal of chlorine abundant isotopologues. Although not mentioned in the text, for this excitation, we have chirped the pulses in order to retrieve the time domain presented for reasons that will become understood in the following part.

6.1 Frequency domain approach and pulse shaping

Up until now we considered the laser pulse as a delta kick and did not pay any attention to the broad spectrum and phase relations of the frequency components as the time domain approach seemed to be more intuitive. In this section, we will briefly explore the excitation in the frequency domain.

The rotational energy ladder is depicted in figure 10, where the eigenenergies are given by $E_J = BJ(J + 1)$ and the corresponding eigenstates are the spherical harmonics.

![Figure 10: The rotational states (levels) of the rotor and their corresponding energies. Resonance energies between adjacent states of the same parity are given in units of the rotational coefficient B.](image_url)

The excitation of the rotational wavepacket may be considered as a sequential Raman process, where successive population transfer between states of $\Delta J = \pm 2$ take place.

The reason for $\Delta J = \pm 2$ comes from the Raman selection rule. A diatomic homonuclear molecule has no permanent dipole and therefore can be excited by Raman process, where the field induces a dipole moment and interacts with it.

Now we go one step further and try to evaluate the nonresonant Raman efficiency for population transfer between $J$ and $J+2$ states. Recall that the laser pulse is centered at $\lambda_c = 800\text{nm}$ with $FWHM \sim 35\text{nm}$.
The nonresonant Raman process can be regarded as the combination of two electric fields resulting in transition to a final state such that: \( \omega_{i\rightarrow f} = \omega_1 - \omega_2 \). The two fields \( \omega_1, \omega_2 \) (pump and dump respectively) must arrive simultaneously because the lifetime of the virtual level is practically zero.

In our case both initial and final states are rotational (\( J \)) states such that \( \Delta J = \pm 2 \) and the corresponding energy difference is generated by pairs of frequencies separated by the 'Raman frequency' \( \omega_{i\rightarrow f} \equiv \Omega \). These frequency pairs originate in our broad pulse spectrum. Furthermore, in such a coherent process, the relative phases of the frequencies are of great importance and the transferred population depends on the phase differences between all of the different pathways of the excitation.

![Diagram of Nonresonant Raman scheme](image)

**Figure 11**: Nonresonant Raman scheme.

![Gaussian pulse spectrum](image)

**Figure 12**: Gaussian pulse spectrum (solid line) and their relative phases for a chirped pulse (dashed line). \( \Omega_0 \) refers to the central frequency of the pulse. Note that the 'ruler' length corresponds to the resonance frequency \( \Omega \).

In our calculation we scan the spectrum using this 'ruler' to get the efficiency of the pulse as a function of \( \Omega \).
\[ E_1(t) = \rho_{(\omega_1)}(e^{i\omega_1t + i\varphi_1} + c.c) \]

\[ E_2(t) = \rho_{(\omega_2)}(e^{i\omega_2t + i\varphi_2} + c.c) \]

\[ E_1E_2(t) = \rho_{(\omega_1)}\rho_{(\omega_2)}(e^{i(\omega_1 + \omega_2)t + i(\varphi_1 + \varphi_2)} + c.c + e^{i(\omega_1 - \omega_2)t + i(\varphi_1 - \varphi_2)} + c.c) \]

Where for a gaussian pulse envelope \( \rho_{(\omega)} = N e^{-\frac{(\omega - \omega_0)^2}{\sigma^2}} \) \( \omega_0 \) - central frequency of the pulse, \( N \) - normalization factor, and \( \sigma \) relates to the width of the spectrum such that \( FWHM = \sigma \sqrt{4\ln(2)} \)

By manipulating the relative phases between the original frequencies of the pulse, we can affect the relative phases of the Raman transition frequencies.

In order to transfer population between two adjacent states with \( \Delta E_{j\to j+2} = \hbar\Omega \) (where \( \Omega \) stands for a specific resonance frequency) we have to take into account all of the frequency pairs in the original pulse, that by mixing together, could generate \( \Omega = \omega_2 - \omega_1 \Rightarrow \omega_2 = \Omega + \omega_1 \).

This is done by integrating over all of the pulse pairs resulting in a difference frequency of the transition frequency \( \Omega \) taking the following integral:

\[ \text{eff} \left( \Omega \right) = \int_{-\infty}^{+\infty} \rho(\omega)\rho(\omega + \Omega)e^{-i\varphi(\omega)}e^{i\varphi(\omega + \Omega)}d\omega + c.c \]

we add all of the relevant pairs scaled with their amplitude and relative phases to get \( \text{eff} \left( \Omega \right) \) which we refer to as the efficiency of the pulse in generating the Raman transition frequency \( \Omega \).

### 6.2 Excitation with Chirped pulses

A Transform Limited (TL) pulse is the shortest pulse (in time domain) for a given spectral bandwidth. This pulse is generated by superposing all frequency components in phase with one another such \( \varphi(\omega) = 0 \ \forall \omega \).

A chirped pulse has the same spectrum, but by applying, a square phase to the frequency components such that \( \varphi(\omega) = K(\omega - \omega_0)^2 \) where K is the chirp factor, results in the lengthening
of the pulse envelope in time domain and in linear shift of the carrier frequency (positive/negative
correlated with the sign of $K$).

We start with calculation of the efficiency of a chirped pulse in generating resonance frequencies.

$$
\text{eff}_{\text{CHIRPED}}(\Omega) = \int_{-\infty}^{+\infty} e^{-\frac{(\omega - \Omega)^2}{\sigma^2}} e^{-iK\omega^2} e^{iK(\omega + \Omega)^2} d\omega + c.c = \sqrt{\frac{\pi}{2}} e^{-\frac{\Omega^2}{2\sigma^2}} (\frac{1}{\sigma^2} + K^2\sigma^2)
$$

For the TL pulse efficiency we set $K=0$

$$
\text{eff}_{\text{TL}} = \sqrt{\frac{\pi}{2}} e^{-\frac{\Omega^2}{2\sigma^2}}
$$

Note that the efficiency does not depend on the central frequency $\omega_0$, and there is no dependence on
the sign of $K$, thus negative and positive chirps are equally efficient. This efficiency function is
basically the effective spectrum for population transfer between rotational states separated by $\Omega$.

Thus, for a given $\Omega$, the transfer efficiency reduces exponentially with increasing $|K|$ (increasing
chirp regardless of sign) and vice versa, for a given $K$, the efficiency decreases exponentially with
increasing $\Omega$. The population transfer efficiency from initial $J$ to $J+2$ as a function of pulse
broadening ratio ($F$) is depicted in the figure 12. Efficiency is given with respect to the TL pulse
efficiency in transferring population between $J=0$ and $J=2$.

![Figure 13: Efficiency of the Raman population transfer from initial J states (to J+2 states) as a function of pulse broadening ratio (F).](image)

K and F are related such that:

$$
K = \frac{D^2 \sqrt{F^2 + 1}}{16 \ln 2}
$$

where $D$ denotes FWHM of the pulse in time domain.
It is clear that as the width of the pulse in time increases, the pulse is less potent for transferring population to higher rotational states.

Chlorine molecules, having significantly higher moment of inertia with respect to nitrogen, are subjected to larger centrifugal distortions, resulting from their initial population at room temperature (centered around J=20) and due to their small difference in energy between the rotational levels. Centrifugal distortions proportional to $D J^2 (J + 1)^2$ become important at the high rotational levels reached in such heavy molecules. The centrifugal distortions results in additional peaks seen in the resolved signal. In order to reduce these 'extra' peaks, a chirped pulse (400 fsec FWHM) was used to measure the Cl$_2$ signal depicted in the article.

Figure 14 depicts FWM signals from Cl$_2$ measured using two pulse widths (100, 700 fsec):

![signal comparison between pulse widths](image)

Figure 14: FWM signal of Cl$_2$ gas using two chirped pulses.

It is clearly seen that the TL pulse (upper panel ~100fs) results in a more complex signal structure while the chirped pulse (lower panel ~700fs) results in the expected double peak signal as expected.
7. Ongoing work and future directions

During my PhD, I had many discussions with my advisors Yehiam Prior and Ilya Averbukh about research directions that would be interesting to pursue. We have already started to consider some of them experimentally and theoretically and will appear in the ongoing work part. Some of the ideas have not been thoroughly considered but I believe they should be included in this thesis for future lab generations to come.
7.1 Spin modifications in symmetric 4 atom molecules

As was shown for diatomic molecules, the time-evolution of rotational wavepackets is nuclear spin selective. For a rotor, states with odd rotational quantum number \( J \) show alignment after a quarter of the revival and states with even \( J \) show anti-alignment.

Acetylene (\( \text{C}_2\text{H}_2 \)) is a linear symmetric molecule, expected to obey to the same spin-rotation constraints discussed for symmetric diatomics. But this four-atom molecule (two atom pairs) offers a much richer playground for the exploration of spin effects. Using these 4 atomic options, one can synthesize several molecular isotopes, differing in their spin functions:

\[
\begin{align*}
^{12}\text{C} & \quad I = 0 \quad \text{Boson} \\
^{13}\text{C} & \quad I = \frac{1}{2} \quad \text{Fermion} \\
^1\text{H} & \quad I = \frac{1}{2} \quad \text{Fermion} \\
^2\text{D} & \quad I = 1 \quad \text{Boson}.
\end{align*}
\]

The isotopomers \( ^{12}\text{C}_2^2\text{H}_2, ^{12}\text{C}_2^2\text{D}_2, ^{13}\text{C}_2^2\text{D}_2 \) and \( ^{13}\text{C}_2^2\text{H}_2 \) demonstrate all binary spin combinations. The spin symmetry and corresponding rotational symmetry depend on the two pairs and should be formulated accordingly. In this project, we calculate and measure the angular behavior based on these more complicated binary spin functions.

When trying to correlate the spin modifications with the rotational wavefunctions (their symmetry / parity), one must take into account the nature of the rotating species (fermions/bosons) and the corresponding statistics they follow. For a diatomic symmetric molecule, this is a fairly easy task.

For a slightly more complicated molecule such as acetylene, these relations are somewhat more demanding. By measuring different atomic combinations and considering their various spin combinations, we explore and the spin-rotation correlation for four-atom, symmetric molecules.

I will present and discuss the experimental results that were already obtained.

In the case of symmetric diatomics, the correlation between the spin wavefunction and the rotational wavefunction was the following:

<table>
<thead>
<tr>
<th>Atomic spin</th>
<th>( \psi_{\text{spin}} )</th>
<th>( \psi_{\text{rotatom}} )</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2} ) (Fermion)</td>
<td>S</td>
<td>Odd ( J )s</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>AS</td>
<td>Even ( J )s</td>
<td>1</td>
</tr>
<tr>
<td>1 (Boson)</td>
<td>S</td>
<td>Even ( J )s</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>AS</td>
<td>Odd ( J )s</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 15: symmetry of spin and rotational wavefunctions for homonuclear diatomics with \( I = \frac{1}{2} \) (fermions) and \( I = 1 \) (bosons).
The case of $\text{C}_2\text{H}_2$ is more interesting since the rotational motion practically exchanges two pairs of atoms (C by C and H by H) together.

Let us start by analyzing the spin functions of $^{13}\text{C}_2\text{H}_2$, since it has two pairs of identical atoms, having non-zero nuclear spin (both $^{13}\text{C}$ and H are fermions with nuclear spin $I = 1/2$).

In order to assign the spin modifications with their odd and even rotational states, one has to divide them to symmetric and anti-symmetric spin functions, and then, depending on their bosonic or fermionic character, correlate them with the rotational state parity. For diatomic homonuclear molecules, this results in $I : I + 1$ population ratio (even:odd – bosons or odd:even – fermions).

For $^{13}\text{C}_2\text{H}_2$, there are 16 optional spin functions, where 4 are totally symmetric, and the other 12 can be symmetrized to give 6 symmetric and 6 antisymmetric. The resulting ratio of symmetric to antisymmetric functions becomes 10:6 or 5:3 ratio. In order to assign the spin functions to rotational states, we have to apply the Pauli principle to the two pairs of atoms separately. In our case, both atomic species are fermions, namely they both require an anti-symmetric total wavefunction upon exchange therefore the total molecular wavefunction must be symmetric upon exchange, just like the bosonic case but with a 5:3 population ratio for even:odd J states.

In order to experimentally confirm the expectations above, we need to somehow discriminate between the odd and even states. This can be achieved by heterodyned measurement of the rotational signal, which reflects the fundamental J state population as discussed above. Due to technical reasons, we have started with a FWM (homodyne) measurement of the acetylenes of interest.

The FWM time and frequency domains of $\text{C}_2\text{H}_2$ are depicted in figure 16, showing the expected rotational evolution where alignment and anti-alignment signals appear at quarter, half and full revival times (similar to the case of nitrogen shown in the upper panel of figure 7).

![Figure 16](image)

Figure 16: (a) Time and (b) Frequency domains measured from $\text{C}_2\text{H}_2$ in the FWM experiment.
The time domain signal seems very similar to the signals obtained from homonuclear diatomics as Nitrogen. Since the FWM signal is background free, the frequency domain does not present the fundamental rotational frequencies as discussed in section 4.2. Instead, one observes binary sums and differences of the fundamental frequencies, from which the actual ratio between even and odd J states cannot be extracted.

By increasing the laser intensity above the multi-photon ionization threshold, we were able to generate a transient grating of plasma in addition to the rotating molecules. The lifetime of the generated plasma, is extremely long with respect to the rotational revival times, typically a few hundreds of picoseconds under our experimental conditions. The probe pulse, scattered off this ‘constant’ weakly ionized plasma grating can be regarded as a local oscillator. The refractive index induced by plasma, is much closer to the refractive index of vacuum, then the refractive indices that may be induced by the molecules regardless of their angular distributions, thus the signal becomes proportional to the absolute square of the refractive index change biased by the constant refractive index arising from plasma. \[ I_{\text{c}}(t) \propto |\Delta n_{\text{rotation}(t)} - \Delta n_{\text{plasma}}|^2 \] (11)

A separate measurement of the plasma lifetime will be presented in section 7.3.

Figure 17 shows a measurement of the combined plasma and rotational grating.

![Figure 17: (a) Time and (b) frequency domains measured from C2H2 in the FWM experiment. The pulses’ intensity exceeds the molecular ionization threshold.](image)

The contribution of the plasma is observed both in the time and frequency domains. In the time domain, it is manifested in a constant background, which can be deduced by comparing the signal before and after the pulse application time. In the frequency domain, we observe mostly the region of fundamental J states. The sums and differences still appear, but they are much weaker with respect to the fundamental peaks.
In figure 18 we compare FWM signals heterodyned by plasma, coming from three acetylene species $^{12}C\_2H\_2$, $^{12}C\_2D\_2$ and $^{13}C\_2H\_2$.

![Figure 18: Time domain FWM measurements heterodyned by plasma formation for the three acetylene isotopomers $^{12}C\_2H\_2$, $^{12}C\_2D\_2$ and $^{13}C\_2H\_2$.](image)

In all three subfigures of figure 18, the pulse intensity exceeds the multiphoton ionization threshold, resulting in a pseudo-heterodyne signal. By comparison, one can clearly observe that the evolution of the alignment factor as a function of time is similar for $^{13}C\_2H\_2$ and $^{12}C\_2D\_2$, judging by the (circled peaks) at the time of quarter revival. The $^{12}C\_2D\_2$ molecule is comprised of two pairs of bosonic constituents, and the $^{13}C\_2H\_2$ constituents are both fermions thus resulting in overall bosonic behavior for both molecules. In $^{12}C\_2H\_2$ one of the pair is bosonic and the other is fermionic, resulting in overall fermionic behavior as expected. Note that in comparison to figure 7 where $^{14}N\_2$ (bosons) are measured, the signal at quarter revival points in the negative direction with respect to the background, opposite to the bosonic case depicted in figure 8. The reason can be found in equation (11), where the refractive index correlated with the plasma grating in much lower then the refractive index of the isotropic case. Thus, the resulting time domain becomes negative with respect to the expected signals. This is clearly observed by looking at the time domain signals around half and full revival of $^{13}C\_2H\_2$, where the signals peak in the opposite direction to the expected one (around half revival, the observed signals first point down and then up).

As for the actual odd and even state population ratio, the quality of data collected until now does not allow the extraction of the actual ratio but further experiments are under way.
7.2 FWM measurement of plasma generation

In order to verify that the constant signal arises from plasma we have measured the intensity of the FWM signal from this ‘constant field source’ as a function of the pulse’s intensity. In a FWM experiment, the signal is proportional to the pulse intensity cube $I_s \propto I_1I_2I_3$. In the following set of measurements, we changed the intensity of the pump-dump pair of pulses and monitored the signal’s intensity.

![Figure 19: Intensity dependence of the FWM signal generated by the plasma grating.](image)

We have found the relation $\frac{I_s}{I_{pr}} \propto (I_{p_1}I_{p_2})^{1.88}$, implying of a multi photon ionization of acetylene leading to the formation of plasma.

Quite interestingly, the number of photons required for ionization is $1.88 \times 2 = 3.76$. Multiplied by the energy per photon of 800nm (12500cm$^{-1}$) we get 47025cm$^{-1}$ which is in very good agreement with literature [88]. Note that ionization may take an alternative path such as tunneling ionization, and require additional aspects, however the good agreement of the required energy with the one stated in literature is worth mentioning in this paper and further exploration is needed. If time permits, I will conduct further experiments with other molecules.
7.3 Plasma lifetime measurement

Since the development of CPA (chirped pulse amplification), ultrashort and ultrastrong laser pulses are available. The peak powers available in table top lab lasers reach tens of Terawatts for a few cycle pulse. These huge laser powers enable research of high energy processes of many kinds. One field, which is constantly evolving, is laser induced plasma and its effect on the electromagnetic field propagating through it. Another hot topic which is tightly connected to plasma formation is the field of filamentation [ref wolf]. In the case of filamentation, an ultrashort laser pulse creates an effective Kerr lense through the third order susceptibility $\chi^{(3)}$. This nonlinear interaction results in the refractive index dependence on the intensity $n = n_0 + n_2 I$. For a laser beam with Gaussian intensity profile, an effective lense is created. This lens affects the actual field that induces it, resulting in the constant focusing of the beam. As the beam focuses it reaches higher and higher peak powers until moltiphoton ionization kicks in, resulting in the generation of weakly ionized plasma which actually behaves as a defocusing beam. The two processes balance each other and result in the channeling of these strong laser pulses and the creation of filaments.

In this section we present some preliminary measurements of laser induced plasma.

In Figure 20 we show the intensity of scattered light from a plasma generated by tightly focusing a laser pulse in air.

![Figure 20: plasma scattering as a function of time](image)

At time 0, a strong ultrashort, tightly focused pulse generates a plasma ball, and a weak pulse coming at 90 degrees is diffracted off this ball. The decay in the scattered probe intensity depends on the plasma density reaching equilibrium (few picoseconds) and from recombination processes, which take long times tens of picoseconds. The slow decay observed for 90 ps in figure 20 can reach several nanoseconds (depending on the experimental conditions). This slow decay was used for heterodyning the FWM signals in the previous section dealing with acetylenes.
7.4 Nano-tube alignment by ultrashort laser pulse

This section deals with laser induced alignment of nanotubes. The calculations shown here have been performed a few years ago, when I started my PhD and with the help of Dr. Ernesto Joselevich. Due to technical difficulties mostly leaning on the disability of transferring the nanotubes to the gas phase, experiments where not performed. However, I believe that this simple idea may be feasible under the right experimental conditions, and even be of importance as an applicable method for separating nanotubes based on their electrical properties.

Nanotubes are usually divided in two groups according to their electrical properties: Semiconductors and metallic. There are no good ways for selective synthesis of one kind, and usually one has to specifically choose the needed kind out of a mixture.

Based on the different electrical properties of the two kinds, we present a scheme for selectivity in addressing one species in a mixture. The idea is based on the alignment of rotors in a strong electric field. We have shown that an ultrashort laser pulse of high power serves to align diatomic molecules, considered as rigid rotors. For diatomic molecules, the most important characteristic time for separation between different species (isotopes) is the quantum revival time, which is of the order of picoseconds (8.3 for N$_2$, ~70 for Cl$_2$ etc.). At these time scales, there is almost no decay due to collisions and multiple revivals are observed. In the case of nanotubes, the quantum revival time is of the order of milliseconds (depending on the length) therefore quantum revivals cannot be observed for nanotubes due to decay processes.

Therefore, we seek for a different characteristic time scale, smaller then the decoherence time of the system that will enable discrimination between the two species of nanotubes. This will be the time needed for the tubes to align for the first time after they are kicked by the ultrashort pulse and will be referred to as the focusing time.

Classical calculation yields a short focusing time, shorter than the decay time of the system, of the order of picoseconds. The difference in the polarizability dependence on length and order of magnitude [89] enables the discrimination between the two species.
7.4.1 Nanotube geometry

We start by considering the geometrical parameters in order to calculate the moment of inertia $(I)$. A nanotube can be regarded as a graphene sheet rolled upon itself. Such a graphene sheet is made of hexagons where in every point there is a carbon atom and a hydrogen atom.

In each unit cell (red rhombus) there are 2 Carbons and 2 Hydrogens. C-C bond length is marked as 'a' where $a=0.144\text{nm}=1.44\text{Å}$.

The area of a unit cell yields:

$$S_{cell} = \sqrt{3}a \times \frac{3}{2}a = \frac{3\sqrt{3}a^2}{2}$$

we consider the following tube of diameter 'd' and length 'L':

$$S_{tube} = \pi d L$$

The number of unit cells is given by:

$$n = \frac{S_{tube}}{S_{cell}} = \frac{\pi d L \times 2}{3\sqrt{3}a^2}$$
The density of the tube per unit length is given by: 
\[ \rho = \frac{n^* M_{\text{cell}}}{L} = \frac{\pi d^* 2}{3\sqrt{3}a^2} \left( \frac{2M_C + 2M_H}{N_A} \right) \]

where \( N_A \) is Avogadro's number.

The moment of inertia:
\[ I = 2\int_0^{L/2} \rho L^2 dL = \frac{\rho L^3}{12} = \frac{\pi d M_{\text{cell}} L^3}{18\sqrt{3}a^2} \]

### 7.4.2 Calculation of the Quantum Revival Time

In this part we calculate the quantum revival time using a rotational coefficient calculated for the nanotube.

\[ B[J] = \frac{\hbar^2}{2I} \quad \text{or in units of} \quad \text{cm}^{-1} \quad B[\text{cm}^{-1}] = \frac{\hbar}{4\pi I c} \]

\[ T_{\text{rev}} = \frac{1}{2 B c} = \frac{\pi^2 d M_{\text{cell}} L^3}{9\sqrt{3}a^2\hbar} \]

In figure 21 we plot the calculated revival time for nanotubes as a function of their length.

![Figure 21: Calculation of the quantum rotational revival time as a function of tube length.](image)

Already for fairly short nanotubes, the revival time is in the microsecond timescale, very long with respect to the decoherence time (~100ps at room temperature), therefore a different time scale is needed.
7.4.3 Evaluation of the classical focusing time

In this part we evaluate the classical focusing time, which is the time passing between the kick experienced by the molecules and the first aligned state. In order to do it, the strength of the kick, time of interaction, and coupling of the electric field and the tubes must be taken into account. Beam waist, temperature and sample’s density are of importance too.

Instead of evaluating all of these parameters, we derive the focusing time through comparison between the nanotube case and the diatomic molecule case measured in the past, using the same experimental system.

We start by writing the equations for the N\textsubscript{2} case:

The rotational energy pumped into the diatomic molecules is given by:

\[ U = \frac{1}{2} \Delta \alpha KE^2 \sin^2(2\theta) = \frac{1}{2} I \omega^2 \]

\( \Delta \alpha \) - Anisotropy polarizability.

\( I \) - Moment of inertia.

\( E \) - Electric field.

\( \omega \) - Angular velocity.

\( K \) - Proportionality constant that takes into account all the parameters of the beam, coupling, time of the pulse etc.

We will calculate \( KE^2 \) for the case of N\textsubscript{2} and use it in the equations for the nanotube.

We can write the angular velocity as:

\[ \omega = \sqrt{\frac{\Delta \alpha KE^2 \sin^2(2\theta)}{I}} = \sqrt{\frac{\Delta \alpha}{I} \times KE^2 \times \sin(2\theta)} \]

In order to derive the focusing time, we use:

\[ \theta = \omega \tau \]

\[ \tau = \frac{\theta}{\omega} = \frac{\theta}{\sqrt{KE^2 \times \sin(2\theta)}} \times \sqrt{\frac{I}{\Delta \alpha}} \]

The focusing time is the time of focusing of molecules regardless of their initial angle \( \theta \).

The angular dependence vanishes for \( \frac{\theta}{\sin(2\theta)} \approx 1 \),

\[ 45 \]
and the focusing time is given by:

$$
\tau_f = \frac{1}{\sqrt{KE^2}} \sqrt{\frac{I}{\Delta\alpha}}
$$

Knowing $\tau_f$, I and $\Delta\alpha$, we can calculate

$$\frac{1}{\sqrt{KE^2}} = \tau_f \sqrt{\frac{\Delta\alpha}{I}}$$

We use our experimental data [ref.] for the calculation of this term.

<table>
<thead>
<tr>
<th></th>
<th>$I [gr* A^2]$</th>
<th>$\Delta\alpha [A^2]$</th>
<th>$\tau_f [fs]$</th>
<th>$\frac{1}{\sqrt{KE^2}} [fs A^2 gr^{-1/2}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>1.407*10^{-23}</td>
<td>1.7404</td>
<td>100</td>
<td>3.517*10^{13}</td>
</tr>
<tr>
<td>$Cl_2$</td>
<td>1.133*10^{-22}</td>
<td>~5</td>
<td>350</td>
<td>7.352*10^{13}</td>
</tr>
<tr>
<td>$O_2$</td>
<td>7.7505*10^{-21}</td>
<td>1.5812</td>
<td>100</td>
<td>1.428*10^{13}</td>
</tr>
</tbody>
</table>

The term $\frac{1}{\sqrt{KE^2}} = \tilde{K}$ can be evaluated as: $4*10^{13} [fs A^{1/2} gr^{-1/2}]$

Now that we have the proportionality factor, we use it for the calculation of the focusing time of the nanotubes, assuming the same experimental conditions.

**Nanotube calculation**

This part will be divided to 2 sections, for the two types available: metallic and semi-conducting. The polarizabilities are taken from [89].

The equivalent equation of motion for the nanotubes is:

$$U = \frac{1}{2} KE^2 \alpha_{zz} L \sin^2 (2\theta) = \frac{1}{2} I \omega^2$$

The focusing time, derived previously is:

$$\tau_f = \tilde{K} \sqrt{\frac{I}{L \alpha_{zz}}}$$

where $\alpha_{zz}$ is the static polarizability in units of $[A^2]$. 

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Semiconducting nanotubes

In the case of the semiconducting nanotube, the static polarizability depends linearly on the tube's diameter and does not depend on the tube's length therefore the interaction is linearly proportional to the length of the nanotube as can be seen from the equation:

\[ \alpha_{zz}^s = \left[ \frac{8\pi\hbar^2e^2}{mA} \right] \left( \frac{1}{2E_g^2} \right) d = 55[A] \times d[A] \]

The resulting focusing time is:

\[ \tau_f = \tilde{K} \times \sqrt{\frac{\pi d M_{cell} L^3}{L \times 55 \times d \times 18 \sqrt{3a^2}}} = \sqrt{\frac{\pi M_{cell}}{55 \times 18 \sqrt{3a^2}}} \times L \]

\[ \tau_f = \tilde{K} \times 1.9535 \times 10^{-13} \times L \sim 8 \frac{fs}{A} \times L[A] \]

We conclude that the focusing time for a semiconducting nanotube is linear with it's length and is evaluated as ~8fs per angstrom.
Metallic nanotube

For the metallic nanotube, we use the same equation for the calculation of the focusing time, but in this case the static polarizability depends strongly on the length of the nanotube [89].

\[ \alpha_{zz}^M = \frac{L^2}{24 \left[ \ln \left( \frac{L}{R} \right) - 1 \right]} \left[ 1 + \frac{\frac{4}{3} - \ln 2}{\ln \left( \frac{L}{R} \right) - 1} \right] \]

For \( L \gg R \), as in the case of nanotubes we approximate the polarizability as:

\[ \alpha_{zz}^M = \text{const} \times L^2 \]

Since the logarithmic dependence in the denominator is slowly varying. This will become important in the focusing time of metallic nanotubes of different lengths. Calculating the focusing time:

\[ \tau_f = \tilde{K} \times \sqrt{\frac{I}{L \alpha_{zz}}} = \tilde{K} \times \sqrt{\frac{\pi dM_{cell} \times \mathcal{V}^3}{18 \sqrt{3} a^2 \times \mathcal{V} \times 7.8 \times 10^{-3} \times \mathcal{V}^2}} \approx 3 \text{ ps} \]

Note that the focusing time for metallic tubes is length independent.

![Figure 22: classical focusing time for semiconducting and metallic nanotubes as a function of their length](image-url)
Figure 22 depicts the focusing time of semiconducting tubes and metallic ones as a function of their lengths. The results of this simplified calculation offer an elegant way for their separation based on their different response to the interaction with the aligning pulse.

The focusing time for semiconducting tubes is linear with their length and may be used for the measurement of their length distribution. Surprisingly, the metallic tubes are found aligned ~3ps after the pulse application regardless of their length. Further interaction with the sample by a strong ionizing pulse in a selective manner may become feasible, as the ionization probability strongly depends on the molecular angular distribution [90].
List of references

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