

## Isotope-selective laser molecular alignment

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We experimentally demonstrate isotope-selective alignment in a mixture of  $^{14}\text{N}_2$ ,  $^{15}\text{N}_2$  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  $^{14}\text{N}_2$ ,  $^{15}\text{N}_2$  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

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

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,  $T_{\text{rev}} = 1/(2Bc)$ . Moreover, as is well known [10], at rational

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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  $|\psi(\theta, T_{\text{rev}} - \tau)\rangle = |\psi(\theta, -\tau)\rangle$ . 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 ( $t \approx T_{\text{rev}}/2$ ), 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.,

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

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

$$(p, q) = (7, 7), (21, 22), (35, 37), \dots \quad (3)$$

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 isotropic 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  $\mu\text{J}$  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<sup>2</sup>. Under these conditions, the rotational energy supplied to a nitrogen molecule by the laser pulse is

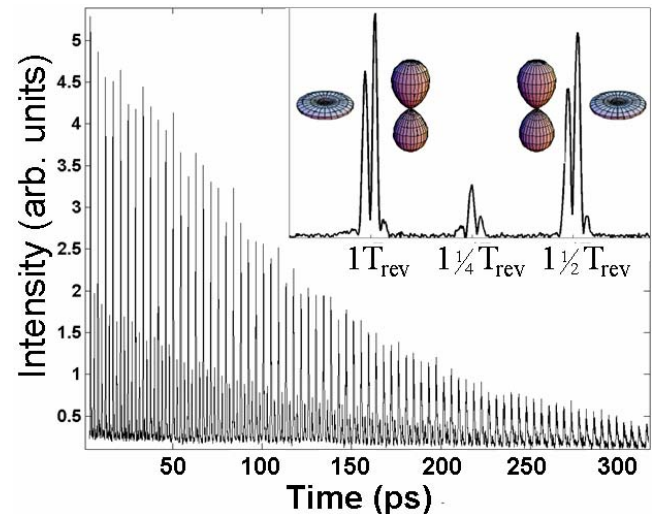


FIG. 1. (Color online) Long scan FWM signal from  $\text{N}_2$  gas (200 torr, room temperature). 40 full revival cycles are shown ( $\sim 320$  ps), where quarter, half and full, revivals are clearly seen. The inset depicts one full revival cycle. Although the FWM signals around full and half revival seem similar, the corresponding angular distributions are reversed [19].

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  $\langle \cos^2\theta \rangle \sim 0.5$  (compared to the isotropic 0.33). The best antialignment is estimated to be of the order of  $\langle \cos^2\theta \rangle \sim 0.2$ . These estimations are consistent with the results of Refs. [11,22], in which a comparable degree of  $\text{N}_2$  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 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  $\sim 63$  ps (region A) and a peak at  $\sim 126$  ps (region B). According to our previous analysis [see Eq. (3)],  $\sim 63$  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  $\sim 126$  ps, the 14th full revival of  $^{15}\text{N}_2$  and the 15th full revival of  $^{14}\text{N}_2$

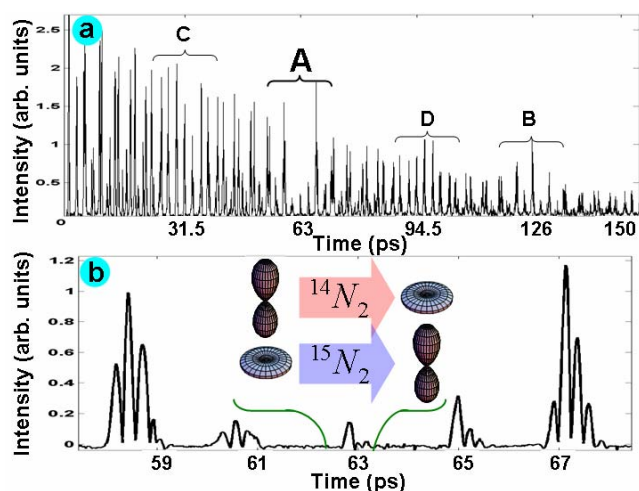


FIG. 2. (Color online) (a) FWM signal from 1:1  $^{14}\text{N}_2$ : $^{15}\text{N}_2$  mixture (500 torr, room temperature). Destructive interference of full and half revival signals is seen in region A at  $\sim 63$  ps; constructive interference of the two full revival signals is observed in region 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.

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 imparted by the second pulse effectively *cancel 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  $^{14}\text{N}_2$  and  $^{15}\text{N}_2$ . As detailed before, at  $\sim 63$  ps,  $^{14}\text{N}_2$  completes 7.5 revival cycles while  $^{15}\text{N}_2$  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

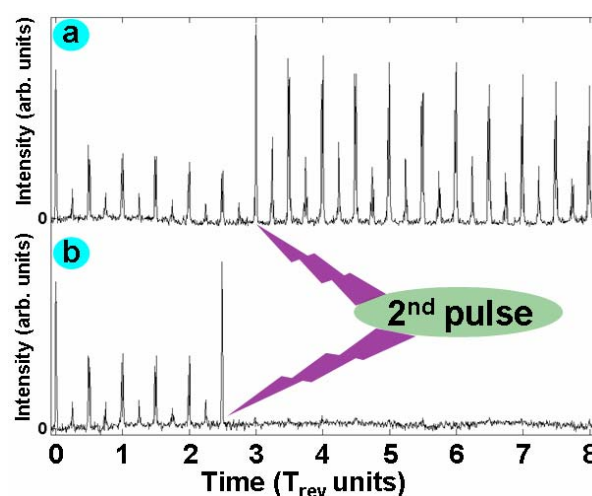


FIG. 3. (Color online) Alignment signal from  $^{15}\text{N}_2$  gas (300 torr, room temperature), following excitation by two pulses. (a) The two pulses are separated by a multiple of the exact revival time ( $3T_{\text{rev}}$ ). The torque from the second pulse adds coherently to that from the first 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.

pulse at  $\sim 63$  ps enhances the alignment of  $^{15}\text{N}_2$  molecules, and almost completely stops the rotation of  $^{14}\text{N}_2$  isotopes.

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 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 in

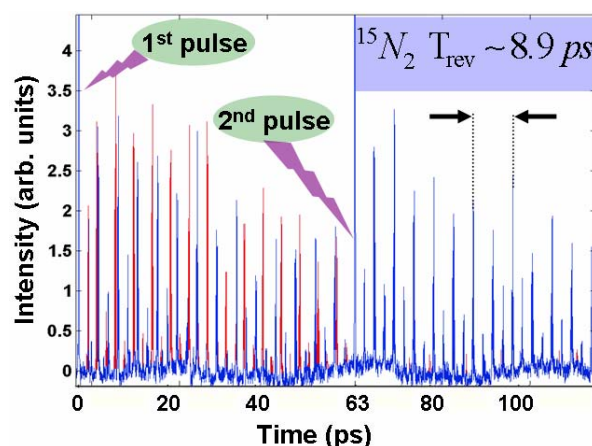


FIG. 4. (Color online) FWM signal from 1:1 mixture of  $^{14}\text{N}_2$ ,  $^{15}\text{N}_2$  (500 torr, room temperature) subject to two pulses (“kicks”), delayed by 63 ps. The first kick excites both molecular isotopes, but the second kick affects them in an opposite way. As a result, after the second 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 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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