Selective Alignment of Molecular Spin Isomers

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(Received 8 May 2007; published 31 August 2007)

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}N) or spin 1 (^{14}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.

DOI: 10.1103/PhysRevLett.99.093002 PACS numbers: 32.80.Lg, 28.60.+s, 32.10.Bi, 42.50.Vk

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., $^{15}N_2$, H_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 $^{14}N_2$ (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 $V(\theta, t) = -(\frac{1}{4})\varepsilon^2(t) \times [(\alpha_\parallel - \alpha_\perp)\cos^2(\theta) + \alpha_\perp]$, where $\varepsilon(t)$ is the envelope of the laser pulse, θ is the angle between the molecular axis and the (vertical) polarization vector of the field, and $\alpha_\parallel$ and $\alpha_\perp$ are the parallel and perpendicular components of the polarizability tensor, respectively. Since typically $\alpha_\parallel \gg \alpha_\perp$, 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, $\langle\langle\cos^2(\theta)\rangle\rangle$ 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 (δ-kick) that is valid for pulses shorter than the typical time of molecular

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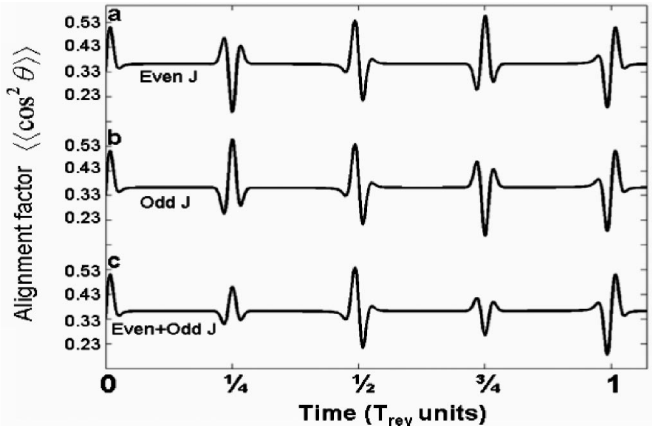

FIG. 1. Time dependence of the alignment factor for (a) para isomers (even J states) and (b) ortho isomers (odd J states), and (c) equilibrium 1:3 mixture of the para/ortho isomers after excitation by a short laser pulse of kick strength $P = 10$.

rotation. The impulse imparted to the molecule is characterized by action (kick) strength $P = (\frac{1}{4}\hbar)(\alpha_\parallel - \alpha_\perp) \times \int_{-\infty}^{\infty} \varepsilon^2(t)dt$. 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 $T_{\rm rev} = 1/2Bc$ 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 ($\frac{1}{4}\,T_{\rm rev}, \frac{3}{4}\,T_{\rm rev}, \ldots$), the ortho and para isomers evolve out of phase: when the para molecules are maximally antialigned (i.e., $\langle\langle\cos^2(\theta)\rangle\rangle$ 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 $\Delta E_{\rm para}$ ($\Delta E_{\rm ortho}$) 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 $\Delta E_{\rm para}/\Delta E_{\rm ortho}$ (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 $\frac{1}{4}T_{\rm rev}$ and $\frac{3}{4}T_{\rm rev}$. 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 $\langle\langle\cos^2(\theta)\rangle\rangle$ value of $\sim$0.7 and $\sim$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 $\frac{1}{4}T_{\rm rev}$ ($\frac{3}{4}T_{\rm rev}$) or just after $\frac{1}{4}T_{\rm rev}$ ($\frac{3}{4}T_{\rm rev}$), respectively. The resulting dramatic difference in the angular distribution sets the stage for the discrimination between the two isomers.

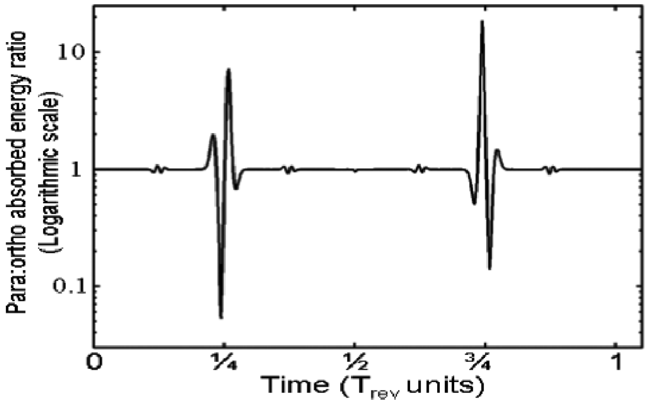

FIG. 2. Double-pulse excitation by two equally strong ($P = 10$) pulses. The selectivity ($\Delta E_{\rm para}/\Delta E_{\rm ortho}$) is plotted as a function of the delay between the pulses.

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 $\vec{k}_1$ and $\vec{k}_2$ 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 μJ pulses from a regeneratively amplified Ti:sapphire laser at 800 nm. The peak field intensity in the focal region was 3×10^{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 [19,20], 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 $\langle\cos^2\theta\rangle \approx 0.5$ (compared to the isotropic 0.33), and the best antialignment is estimated to be of the order of $\langle\cos^2\theta\rangle \approx 0.2$. 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 the ortho and para isomers [as depicted in Fig. 1(c)] is clearly visible. After the second pulse (applied around $1\frac{1}{4}T_{\rm rev}$), 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, $1\frac{1}{4}T_{\rm rev}$ 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.

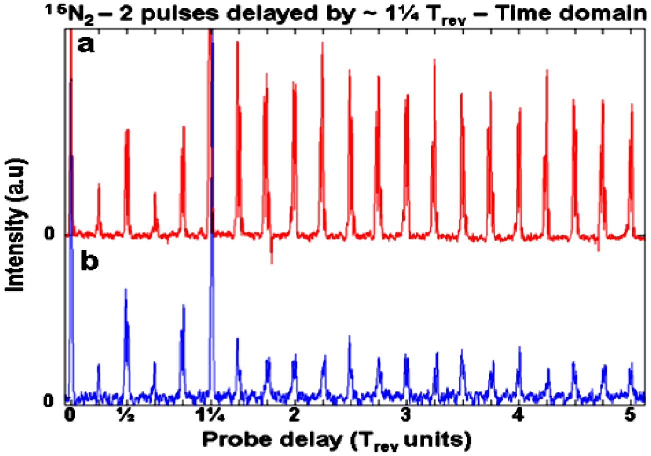

FIG. 3 (color online). Time domain FWM signal from doubly excited $^{15}N_2$. The second pulse was applied (a) just before, (b) just after $1\frac{1}{4}T_{\rm rev}$. Note that the second pulse was applied at $1\frac{1}{4}T_{\rm rev}$ (instead of the practically identical time of $\frac{1}{4}T_{\rm rev}$) to clearly demonstrate the "before" and "after" second pulse signals.

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 ~150 fsec after $\frac{3}{4}T_{\rm rev}$ 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 $1\frac{1}{4}T_{\rm rev}$ where only J states of the same parity are excited. The dashed line (11.12 psec, just before $1\frac{1}{4}T_{\rm rev}$) corresponds to the selective excitation of para molecules (even J states), and the solid line (11.38 psec, just after $1\frac{1}{4}T_{\rm rev}$) corresponds to the selective excitation of ortho molecules (odd J states). The intensity difference between

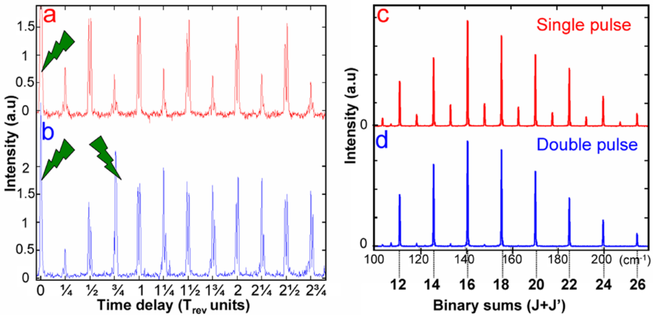

FIG. 4 (color online). Time domain FWM signal from $^{15}N_2$ excited by (a) a single pulse and (b) two pulses delayed by $\sim\frac{3}{4}T_{\rm rev}$. Figures (c) and (d) are the Fourier transforms of (a) and (b), respectively. The depicted $J + J'$ range corresponds to the most intense FWM spectral lines resulting from excitation of the initial thermal ensemble.

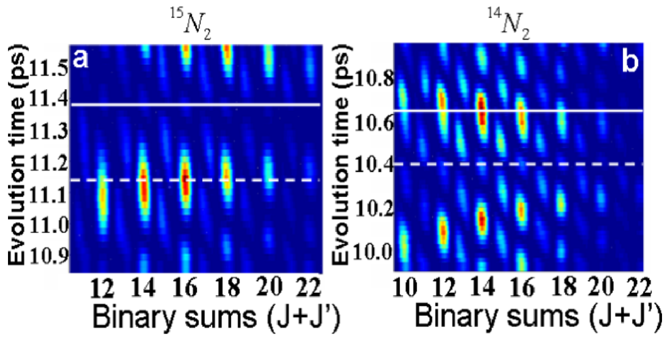

FIG. 5 (color online). Fourier Transform of 2D FWM scan for (a) $^{15}\mathrm{N}_2$ and (b) $^{14}\mathrm{N}_2$ molecules. The vertical axis is the delay time between the pulses (around $1\frac{1}{4}T_{\mathrm{rev}}$), and the frequency in the horizontal axis is expressed in terms of the binary sums ($J + J'$).

the two lines stems from population ratio 3:1 for ortho/para isomers of $^{15}\mathrm{N}_2$.

Figure 5(b) presents similar data for $^{14}\mathrm{N}_2$ (two Bosonic atoms with nuclear spin $I = 1$). Here, the Fourier peaks are weak before $1\frac{1}{4}T_{\mathrm{rev}}$(dashed line, 10.4 psec) and strong after $1\frac{1}{4}T_{\mathrm{rev}}$(solid line, 10.6 psec). Unlike $^{15}\mathrm{N}_2$, in $^{14}\mathrm{N}_2$ 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 $^{14}\mathrm{N}_2$ 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.

This work was supported in part by the Nancy and Steve Grand Center for Sensors and Security, the Israel Science Foundation, and by Israel Ministry of Science Culture & Sport. This research is made possible in part by the historic generosity of the Harold Perlman Family.

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