Quantum Resonances in Selective Rotational Excitation of Molecules with a Sequence of Ultrashort Laser Pulses

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We experimentally investigate the effect of quantum resonance in the rotational excitation of the simplest quantum rotor—a diatomic molecule. Using the techniques of high-resolution femtosecond pulse shaping and rotational state-resolved detection, we measure directly the amount of energy absorbed by molecules interacting with a periodic train of laser pulses, and study their dependence on the train period. We show that the energy transfer is significantly enhanced at quantum resonance, and use this effect to demonstrate selective rotational excitation of two nitrogen isotopologs, $^{14}N_2$ and $^{15}N_2$. Moreover, by tuning the period of the pulse train in the vicinity of a fractional quantum resonance, we achieve selective rotational excitation of *para*- and *ortho*-isomers of $^{15}N_2$.

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The periodically kicked rotor is a paradigm system for studying classical and quantum chaos [1]. In the quantum regime, the dynamics of the kicked rotor exhibits such fundamental phenomena as suppression of classical chaos [1], Anderson localization in angular momentum [2,3], and quantum resonances in the accumulation of rotational energy [4]. Even though these effects have been thoroughly studied with ultracold atoms in optical fields [5] and Rydberg atoms in microwave fields [6], they have never been observed experimentally in a real rotational system.

It has been recently indicated [7] that quantum resonances can be detected and explored in a system of true quantum rotors—an ensemble of diatomic molecules subject to periodic rotational kicking by ultrashort nonresonant laser pulses. It has been also proposed to use this quantum effect for selective laser manipulation of molecular mixtures [7]. Here, we demonstrate for the first time the fundamental phenomenon of quantum resonance in a real rotational system by studying the transfer of energy from a femtosecond pulse train to the rotation of different isotopologs of molecular nitrogen. We start with rotationally cold molecules and measure the energy transfer directly by means of a state-resolved detection of the rotational population in the excited molecular ensemble. To generate a train of ultrashort pulses, we use a high-resolution femtosecond pulse shaper which enables us to scan the train period on the revival time scale. In our experiments, quantum resonance is manifested by a strong dependence of the population distribution width and the acquired rotational energy on the pulse train period with a sharp maximum at the rotational revival time.

Following the proposal of [7], we also demonstrate isotope-selective rotational control in a mixture of $^{14}N_2$ and $^{15}N_2$ by tuning the train period near the quantum resonance, and spin-selective control in a mixture of different spin isomers of $^{15}N_2$ by kicking the molecules near the fractional quantum resonance.

Strong laser fields affect molecular rotation by exerting an angle-dependent torque on the field induced molecular dipole [8–13]. The interaction is described by the potential $U(\theta, t) = -\frac{1}{4}\Delta\alpha E^2(t)\cos^2\theta$, where $\Delta\alpha$ is the anisotropy of the molecular polarizability, $E(t)$ is the electric field envelope, and θ is the angle between the molecular axis and field polarization. In the limit of ultrashort laser pulses, the pulse acts on a molecule as an instantaneous rotational "δ kick". In the quantum picture, a laser kick induces multiple Raman transitions between the rotational states of the molecule, transferring population from lower to higher rotational states and creating a coherent rotational wave packet—a quantum-mechanical analog of the ensemble of classical rotors. Because of the discrete energy spectrum of the rotational wave packet, its dynamics is periodic in time, with a period known as the rotational revival time [14]. Rotational revivals have been thoroughly studied in the context of molecular alignment [11,12]—the appearance of a preferential direction in the distribution of molecular axes [15].

Quantum periodicity of the rotational dynamics raises the question about the ability to enhance, and possibly control, molecular rotation with a periodic sequence of laser pulses (a "pulse train") [16]. An accumulative effect of a pulse train on the degree of molecular alignment has indeed been observed when the train period exactly matched the revival time [17], yet the direct measurement of the degree of rotational excitation and its dependence on the train period have not been studied. Here, we detect the total energy transfer between the optical field and the molecules, showing that the accumulation of rotational energy in the molecular species resonant with the applied pulse train is substantially higher than in the off-resonance molecules.

Understanding the dynamics of molecules driven by periodic laser fields in the context of periodically kicked rotor may offer new tools for numerous schemes of coherent control of chemical reactions [18,19], laser cooling and trapping of molecules [20], control of molecular collisions [21], deflection of molecular beams [22,23], high harmonic generation [24,25], and molecular scattering from surfaces [26,27]. The rotational revival time, being proportional to the molecular moment of inertia, is different for different molecules even if their chemical structures are identical, as in the case of molecular isotopologs. Differences in revival times have been used to selectively align a single species in a mixture of molecular isotopologs [28] by utilizing constructive and destructive interference in rotational excitation by a pair of short laser pulses [29]. Quantum resonance provides an alternative approach to selective coherent control of molecular rotation in mixtures [7].

Our experimental setup is depicted in Fig. 1(a). Cold nitrogen was produced by a supersonic expansion from a pulsed valve nozzle (Even-Lavie valve, EL-5-C-S.S.-2010). After entering the second chamber through a 1-mm diameter skimmer, the molecules were excited by a femtosecond pulse train and probed by a resonance-enhanced multiphoton ionization (REMPI) with a second narrow band pulse. The ions were extracted with a time-of-flight apparatus and the total ion signal was measured with a microchannel plate detector. To block the detector from the ions induced by the excitation field, probe pulses were focused downstream from the excitation region and delayed by 100 ns to account for the molecular motion between the two spots. The ion signal was averaged over 20 pulses.

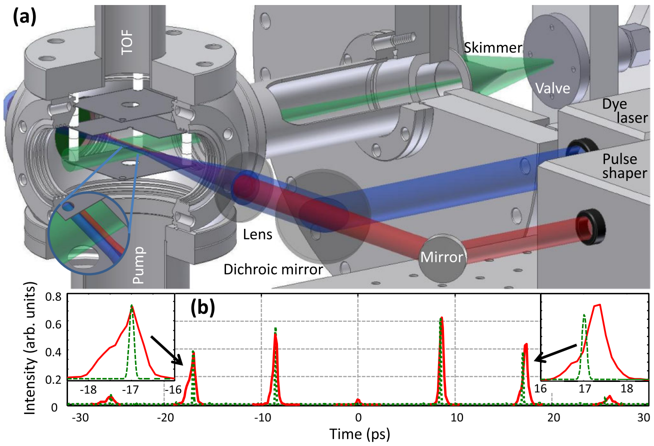

FIG. 1 (color online). (a) Experimental setup. Cold nitrogen molecules from a supersonic expansion enter the detection chamber through a 1-mm diameter skimmer. The rotational temperature of 6.3 K, calculated from the REMPI spectrum, determines the initial rotational distribution. The molecules are excited by a femtosecond pulse train produced with a pulse shaper (red narrow beam) and ionized 100 ns later with a narrow band UV pulse (blue wide beam) shifted downstream with respect to the excitation pulse. The ions are extracted and detected with a standard time-of-flight (TOF) apparatus. (b) Example of the intensity envelope of a pulse train implemented in this work ($A = 2.5$, $\tau = 8.5$ ps). Measured (red solid line) and calculated (green dashed line) intensity profile. The insets show the discrepancies attributed to the finite optical resolution of the shaper.

The excitation pulse train was obtained by phase-only shaping of a linearly polarized 600 μJ pulse that originated from a regenerative amplifier (Spectra-Physics, Spitfire, 2 mJ at 1 kHz repetition rate). We used a home built $4f$ Fourier pulse shaper [30] based on a 640-pixel liquid crystal spatial light modulator (SLM-640, Cambridge Research and Instrumentation, Inc.). To avoid strong multiphoton ionization of nitrogen by the femtosecond train, the shaper was slightly misaligned for stretching the pulses from 150 to about 500 fs. Sinusoidal phase modulation $\phi(\omega) = A \sin[(\omega - \omega_0)\tau]$ was applied to the input pulse spectrum to create a pulse train in the time domain, $E(t) = \sum_{n=-\infty}^{\infty} J_n(A)\varepsilon(t + n\tau)$, where $\varepsilon(t)$ and $E(t)$ represent the electric field envelopes of the input (in our case, nearly Gaussian) pulse and output pulse, respectively, A is the spectral phase modulation amplitude, $J_n(A)$ is the Bessel function of the first kind, τ is the train period, and ω_0 is the carrier frequency of the input field. High resolution of the shaper ($\Delta\lambda = 0.04$ nm/pixel) allowed us to produce pulse trains of seven pulses with a period of up to 10 ps. An example of a pulse train (both calculated and measured) with $A = 2.5$ and $\tau = 8.5$ ps is shown in Fig. 1(b). Because of the finite resolution of the shaper, the end pulses at ±17 and ±26 ps are slightly distorted, but are still shorter than the rotational period of N_2 in the highest rotational state ($J = 7$) accessible with the available total pulse energy of 190 μJ after the shaper. To achieve the high laser intensity required to drive multiple Raman transitions between the rotational levels, pump and probe beams were focused by a 150 mm focal length lens. After measuring the focal spot size, the pump laser intensity was estimated on the order of 5×10^{12} W/cm^2, which corresponds to the dimensionless total kick strength $P \approx 7$. The total kick strength is the typical amount of angular momentum (in units of $\hbar$) transferred from the field to the molecule, and is defined as $P = (\Delta\alpha/4\hbar)\int E^2(t)dt$ [31].

The rotational distribution was probed by narrow band nanosecond pulses from a tunable dye laser (Sirah PrecisionScan, 2 mJ at 283 nm and 10 Hz repetition rate). Nitrogen molecules were ionized via a "2 + 2" REMPI, with a two-photon resonant transition $a\ {}^1\Pi_g(v' = 1) \leftarrow X\ {}^1\Sigma_g^+(v'' = 0)$. The frequencies of the S-branch transitions ($\Delta J = 2$) are well separated, allowing us to detect the population of the first eight rotational levels $J'' = 0, 1, \ldots, 17$ of the ground electronic state. The detection method does not offer resolution in time, but provides spectral resolution for identifying individual rotational states. The number of observed rotational states is in good agreement with the estimated dimensionless kick strength P, which sets an upper bound for the highest expected excitation. The REMPI spectrum of $^{14}N_2$ molecules before and after the application of the excitation laser field is shown in Fig. 2.

To measure the total rotational energy absorbed by the molecules, we detected the transfer of population from the initially populated ($J'' = 0, 1, 2$) to higher ($J'' \leq 7$) rotational states as a function of the pulse train period. REMPI signal was measured by tuning the probe wavelength to the corresponding peak of the REMPI spectrum, and recording the ion signal while scanning the train period with the pulse shaper. To determine the relative population of each rotational level, $S_{J''}$, REMPI signals were scaled with the corresponding two-photon line strength factors for the $J' \leftarrow J''$ rotational transitions and the nuclear spin degeneracy weights [32]. The results are shown in Fig. 3(a). The highest increase of rotational energy (i.e., the most efficient population transfer up the rotational ladder) occurs around 8.4 ps—the revival time of $^{14}N_2$, where the population is efficiently transferred from the lower to higher angular momentum states, as indicated by the dips and peaks in $S_{0,1}$ and $S_{2,...,7}$, respectively. The small drop of the total population ($\sum_{J''} S_{J''}$) below unity away from quantum resonance can be attributed to the resonance-enhanced anisotropy of the spatial distribution of the molecular angular momentum, which was not taken into account in our conversion of the REMPI signal to the relative populations. The energy of a molecule is calculated as the sum of rotational energies weighted by the corresponding populations. In Fig. 3(b), the total energy absorbed by the molecules, i.e., the difference of rotational energy before and after the excitation, is plotted as a function of the dimensionless detuning from quantum resonance, $\epsilon = 2\pi[\tau/T_{\text{rev}} - 1]$. Both plots, for $\epsilon < 0$ and $\epsilon > 0$, closely resemble the characteristic oscillating behavior predicted in [7]. Because of the diffusion of molecules in and out of the sample volume during the time between the excitation and probe pulses, Fig. 3 shows the lower limit of the absorbed energy.

To emphasize the resonant nature of the rotational energy accumulation by the molecules, we normalized the ion signal for each J'' separately [i.e., we divided each curve in Fig. 3(a) by its maximum value] and plotted the results as a two-dimensional map in Fig. 4(a). The effect of quantum resonance is clearly demonstrated by the significantly enhanced population transfer to higher J states when the period of the femtosecond pulse train matches the rotational revival time. Remarkably, even for a relatively small number of pulses in the train (see Fig. 1), the observed resonance is quite narrow and can be used for selective rotational excitation of molecular mixtures. We demonstrate this by performing the same measurement with two isotopologs of nitrogen, which have identical chemical structure but different rotational properties, reflected by the difference in the revival time. The detected population transfer efficiency for $^{14}N_2$ ($T_{\text{rev}} = 8.38$ ps) and $^{15}N_2$ ($T_{\text{rev}} = 8.98$ ps) is shown in Figs. 4(a) and 4(c), respectively. By tuning the pulse train period to 8.4 or 9.0 ps, one can induce the rotation of a selected isotopolog, while keeping the other in its initial rotational state.

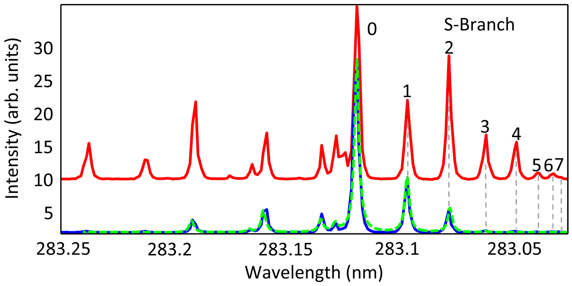

FIG. 2 (color online). Normalized REMPI spectra of $^{14}N_2$. Relevant peaks of the S branch are labeled by the corresponding J'' numbers. Before the application of a femtosecond pulse train, the distribution of rotational population is thermal and corresponds to 6.3 K (lower solid blue line—experiment, green dashed line—calculations [35]). At this temperature, only $J'' = 0$, 1, and 2 are populated significantly. An example of the REMPI spectrum of rotationally excited molecules is shown by upper solid red line. For a total laser kick strength used in our experiments, states up to $J'' = 7$ are populated.

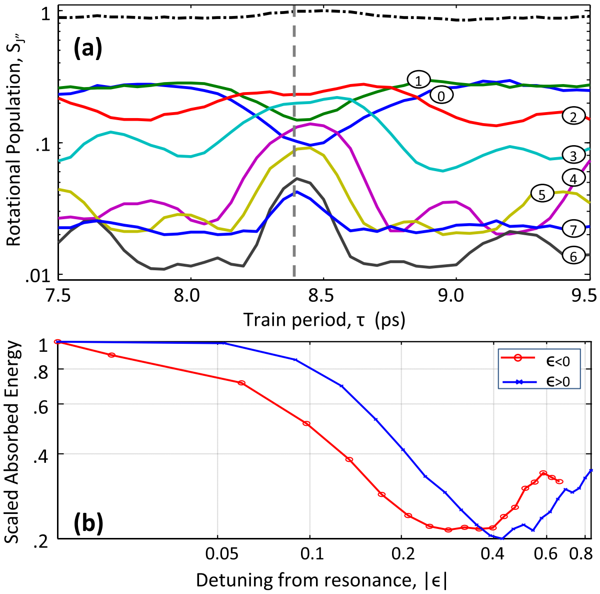

FIG. 3 (color online). (a) Relative populations $S_{J''}$ of the rotational levels of $^{14}N_2$ as a function of the pulse train period. Each curve is labeled with the corresponding rotational quantum number $0 \leq J'' \leq 7$. Vertical dashed line marks the rotational revival time, at which the efficiency of the rotational excitation by a periodic train of pulses is significantly enhanced. Total population, $\sum_{J''} S_{J''}$, is depicted by the upper dash-dotted line. (b) Total absorbed energy, normalized by its resonant value, as a function of the dimensionless detuning from quantum resonance (see text).

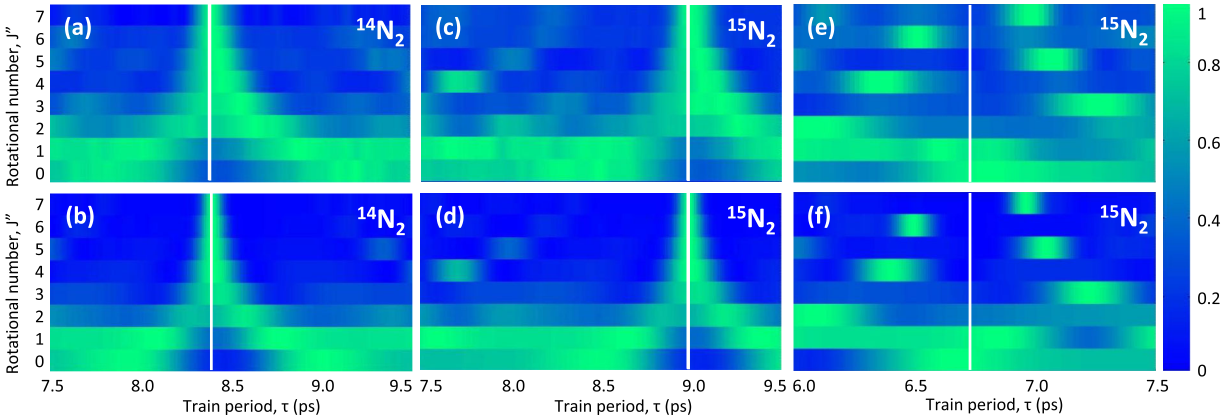

FIG. 4 (color online). Experimental results (upper row) and numerical simulations (bottom row) of a normalized REMPI signal (color coded) for different J'' states as a function of a pulse train period. Left and middle columns correspond to $^{14}N_2$ and $^{15}N_2$, respectively. For a pulse train period equal to the revival time (white vertical lines) the population is efficiently transferred from the initial states $J'' = 0, 1, 2$ to the higher states $J'' = 3, 4, \ldots, 7$. Right column shows the rotational population distribution for $^{15}N_2$ as a function of the pulse train period around $\frac{3}{4}T_{\mathrm{rev}}$ (white vertical line).

The results of numerical calculation of the rotational population transfer for both isotopologs are shown in the bottom row of Figs. 4(b) and 4(d). In our simulations, we averaged over the fast oscillations of the electric field, expanded the wave function in the spherical harmonics, and solved numerically the time-dependent Schrödinger equation to obtain the expansion coefficients [7]. The actual shape of the generated pulse trains has been included in the calculations. To take into account thermal effects, we averaged over the initial states, where each result is weighted by the Boltzmann coefficient (including nuclear spin statistics) of the initial state.

Molecular spin isomers, such as *para*- and *ortho*-isomers of $^{15}N_2$, exhibit identical revival times yet different structure of rotational levels. *Para*-nitrogen (total nuclear spin $I = 0$) does not have odd J states in its rotational spectrum, whereas even J's are missing in the spectrum of *ortho*-nitrogen (total nuclear spin $I = 1$). *Para*- and *ortho*-isomers coexist in our gas sample in the proportion of 1:3. In this case, coherent control of molecular rotation can be based on fractional, rather than full, rotational revivals. An example is shown in Figs. 4(e) and 4(f) (experiment and theory, respectively), where selective population transfer into even (odd) excited rotational states of *para*- or *ortho*-nitrogen is achieved by tuning the period of the femtosecond pulse train slightly below (above) $\frac{3}{4}T_{\mathrm{rev}}$. We note that, unlike the selectivity of molecular alignment demonstrated with a sequence of two pulses [33,34], our results suggest that pulse trains may offer a new way of state-selective excitation of high rotational states. With a relatively small number of pulses used here, the selectivity is limited to low lying J'' states (e.g., $J'' = 4$ at $\tau \approx 6.3$ ps or $J'' = 5$ at $\tau \approx 7.1$ ps).

In summary, the periodically kicked quantum rotor was studied experimentally and theoretically, using nitrogen molecules and a train of ultrashort laser pulses. Quantum nonlinear resonances have been demonstrated in the efficiency of rotational excitation as a function of the pulse train period. Enhancement of the rotational energy transfer has been observed at and around full and fractional revivals of the molecular quantum wave packet. The ability to use quantum resonances for the selective excitation of different molecular isotopologs and nuclear spin isomers has been shown.

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