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Control of rotational wave-packet dynamics in asymmetric top molecules

Lotte Holmegaard,[1] Simon S. Viftrup,[2] Vinod Kumarappan,[1] Christer Z. Bisgaard,[2,*] and Henrik Stapelfeldt[1,†]
[1]*Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark*
[2]*Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*

Edward Hamilton[3] and Tamar Seideman[3,‡]
[3]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA*
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We combine newly developed experimental and theoretical methods to explore and control the rotations of asymmetric top molecules. In the low-temperature limit, the revival spectra of laser-driven rotational wave packets exhibit a fascinating quantum-mechanical structure, which is qualitatively different for asymmetric tops compared to symmetric or linear tops. With increasing fluence, the structure gradually simplifies, illustrating a controllable transformation of the rotational dynamics. Our theoretical and experimental predictions are in qualitative agreement.

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Irradiation of molecules by femtosecond or picosecond laser pulses can form broad, coherent superpositions of rotational states if the pulse intensity is high enough to induce a sequence of stimulated rotational transitions, yet low enough to avoid multiphoton or tunnel ionization [1,2]. Such rotational wave packets have attracted rapidly increasing interest over the past five years, fueled by new exciting possibilities in a number of areas such as rotational spectroscopy [3], quantum logic [4], ultrafast imaging [5,6], and chemical control [7]. These and other opportunities rely on the short duration of the pulse, which offers an approach to creating ensembles of spatially aligned molecules after the laser pulse has been turned off; hence, aligned molecules free of disturbances from the alignment field.

Alignment results from interference among the eigenstates forming the rotational wave packet. In the specific case of a linearly polarized, nonresonant laser pulse, the most polarizable molecular axis aligns along the polarization direction shortly after the pulse and at subsequent wave-packet revivals. For linear molecules, which have been the subject of the vast majority of studies to date, the revival pattern is periodic, as expected for a wave packet of discrete levels that corresponds to regular motion in the classical limit. Here, experimental observables exhibit alignment transients at integer multiples of $1/2B$ (B is the rotational constant expressed in frequency units) and at fractions thereof. Symmetric top molecules also have discrete regular spectra and exhibit similar revivals, although having an additional structure, due to the availability of two rotation axes. Asymmetric top molecules display much more interesting rotational dynamics. The corresponding classical motion is unstable, translating into a rich, nonperiodic revival spectrum in the quantum domain [2]. In addition to the fundamental interest in the complex rotational revivals of asymmetric top molecules, there is growing practical interest in understanding the potential of creating field-free alignment in asymmetric tops, as most molecules are asymmetric. To date, however, the alignment dynamics and revival pattern of asymmetric tops have been explored only in very few studies [8–13].

The purpose of the present work is threefold. First we illustrate numerically that increasing the fluence (intensity times duration) F_{align} of the alignment pulse introduces an interesting simplification of the rotational revivals, effectively converting the complex, nonperiodic or quasiperiodic rotations of an asymmetric top to a simple periodic pattern. This effect, experimentally unobserved so far, is shown theoretically to obtain for molecules of widely differing asymmetries. Since the degree of rotational excitation in the short-pulse domain is determined by the laser fluence [2], the transformation from the nonperiodic to the periodic revival spectrum can be affected by either increase of the intensity [11] or increase of the pulse duration, introducing a new tool for control of molecular rotations. Next we use a recently developed experimental setup [14] to reduce the rotational temperature T_{rot} to a domain that was not explored in previous alignment experiments. The low rotational temperature, combined with a spatially confined probe, allows us to observe quantum-mechanical structure that was analyzed numerically in the past [15] but was never observed in the laboratory. Using iodobenzene as an example, we demonstrate a dramatic change of the rotational revival pattern by gradually increasing the fluence: At low fluence the rotational dynamics is entirely dominated by quasiperiodic J-type revivals corresponding to quasi-symmetric-top-like rotation. By contrast, at high fluence the J-type revivals are almost completely suppressed and replaced by strong, periodic C-type revivals corresponding to the molecule rotating around an axis perpendicular to the molecular plane. Finally, we repeat the calculations at the set of parameters pertaining to our experiments, illustrating qualitative agreement between the experimental and numerical results.

Our theoretical and experimental methods have been described before [1,2] and only the new features of the experimental setup are included here. A pulsed molecular beam, formed by expanding a mixture of 5 mbar iodobenzene and

*Present address: Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada K1A 0R6.
†Electronic address: henriks@chem.au.dk
‡Electronic address: seideman@chem.northwestern.edu

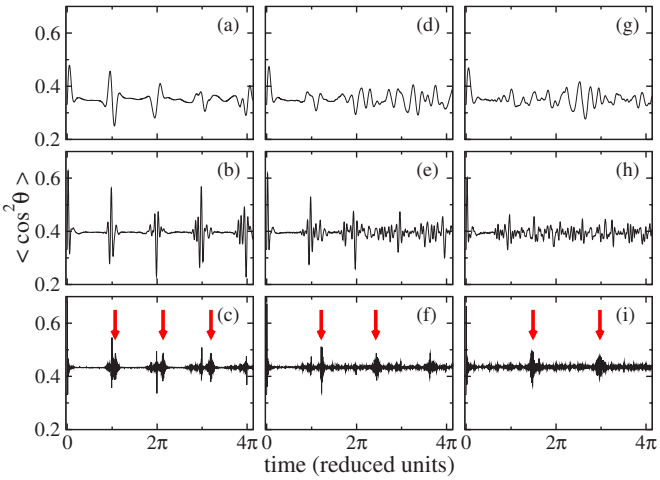

FIG. 1. (Color online) Computed revival spectra for an asymmetric top molecule vs the dimensionless time parameter $\bar{t}=(\hbar/\bar{I})t$. The three columns are obtained for $\kappa=-0.965$ (left), -0.90 (middle), and -0.80 (right). $T_{\mathrm{rot}}=0.4$ K and $\tau_{\mathrm{align}}=0.71$ ps. The fluences (peak intensities) in the upper, middle, and lower rows are 0.14 J/cm^2 (2×10^{11} W/cm^2), 0.71 J/cm^2 (1×10^{12} W/cm^2), and 4.2 J/cm^2 (6×10^{12} W/cm^2), respectively. The arrows mark the positions of the *C*-type revivals (see text).

100 bar helium into vacuum, is crossed at 90° by two pulsed laser beams. The first laser beam induces alignment of the iodobenzene molecules. Its pulse duration τ_{align} is tunable in the range 0.15–4.0 ps full width at half maximum by means of a grating stretcher and its intensity is varied using a half-wave plate in front of a polarizer. The second laser beam is spectrally broadened in a hollow capillary and recompressed to 25 fs. It is used to probe the molecular orientation by Coulomb exploding the iodobenzene molecules. Its intensity is fixed at 2.5×10^{14} W/cm^2. Both laser beams are focused onto the molecular beam by a 30-cm-focal-length lens. The spot size of the alignment beam ($\omega_0^{\mathrm{align}}=45$ μm) is adjusted to be significantly larger than that of the probe beam ($\omega_0^{\mathrm{probe}}=25$ μm).

At the intensity of the probe pulse employed here, a major fraction of the Coulomb explosion events leads to production of I^+ ions with either a $C_6H_5^+$ or a $C_6H_5^{2+}$ partner ion. The mutual electrostatic repulsion causes an I^+ ion to recoil along the symmetry (C_2) axis of its parent molecule. Since the dissociation time is much faster than the rotational periods, the spatial orientation of the molecular C_2 axis at the arrival time of the probe pulse can be determined by recording the direction of the I^+ ion. This is done using a two-dimensional ion imaging spectrometer [14].

In Fig. 1, the transition between the weak and the strong field rotational revivals is shown for three different values of the asymmetry parameter $\kappa=-0.965$ (corresponding to iodobenzene) [Figs. 1(a)–1(c)], -0.90 [Figs. 1(d)–1(f)], and -0.80 [Figs. 1(g)–1(i)], where $\kappa=(2B-A-C)/(A-C)$ is an asymmetry parameter that approaches -1 in the prolate symmetric top limit. To clarify the physical content of the revival features we use reduced time units $\bar{t}=(\hbar/\bar{I})t$ [2] where $\bar{I}$ is the average of the moments of inertia along the molecular *a*- and *b*-axes. The polarizability tensor is kept fixed and chosen

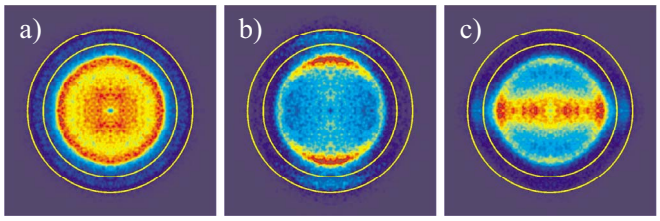

FIG. 2. (Color online) I^+ ion images obtained (a) without the alignment pulse, and (b), (c) with a 0.2-ps-long alignment pulse ($F_{\mathrm{align}}=3.3$ J/cm^2). In (b) the molecules align at $t=351.0$ ps, corresponding to the maximum of the half *J*-type revival. In (c) the molecules anti-align at $t=702.0$ ps corresponding to the minimum of the full *J*-type revival. The probe and alignment pulses are polarized perpendicular and parallel (vertical) to the image plane. The circular rings mark the (I^+, $C_6H_5^{2+}$) channel (see text).

identical to that of iodobenzene to simplify the connection to our experimental results. Likewise the moments of inertia in the first row [Figs. 1(a)–1(c) correspond to those of iodobenzene, whereas the second [Figs. 1(d)–1(f)] and third [Figs. 1(g)–1(i)] rows are obtained by varying the relative values of *B* and *C* while keeping the trace of the inertia tensor constant.

The low fluence limit seen in Figs. 1(a), 1(d), and 1(g) corresponds to the structure of a rotational coherence spectroscopy (RCS) trace [3,16]. Close to the prolate symmetric top limit, these revivals appear approximately at integer multiples of π, and are classified as *J*-type revivals in the RCS literature. As the fluence increases [Figs. 1(a)–1(c)], the *J*-type features diminish and a new set of regularly spaced revivals become pronounced. These features are controlled by coherences arising from transitions between the lowest-energy states for a given value of the total angular momentum, as split by the asymmetric top *K* coupling in the free rigid rotor Hamiltonian, and are therefore uniquely associated with asymmetric tops. As the intensity of the alignment pulse increases and higher *J* levels are excited, these features become more prominent.[1] In the RCS context, similar features were shown to grow in prominence as the asymmetry increases and were termed *C*-type revivals [17]. Here, the *C*-type-like features arise from multiple-level (rather than pairs of levels) interferences, and their physical origin differs from that in the RCS case, but their appearance is very similar. Importantly, they are characterized by the simple regularly spaced patterns ($1/4C$ periodicity) that were noted in the RCS literature [16,17].

Figure 2 introduces our experimental method of probing the alignment, showing examples of I^+ ion images resulting from Coulomb explosion of iodobenzene. When only the probe pulse is used, a circularly symmetric image is obtained [Fig. 2(a)]. This is consistent with our expectation for a sample of unaligned molecules. Also, images are shown where the C_2 axes of the molecules are aligned along the polarization vector of the alignment pulse [Fig. 2(b)] or anti-aligned in the plane perpendicular to the alignment pulse polarization [Fig. 2(c)].

[1]Reference [11] also provides an explanation of the change in the rotational revivals as the intensity increases.

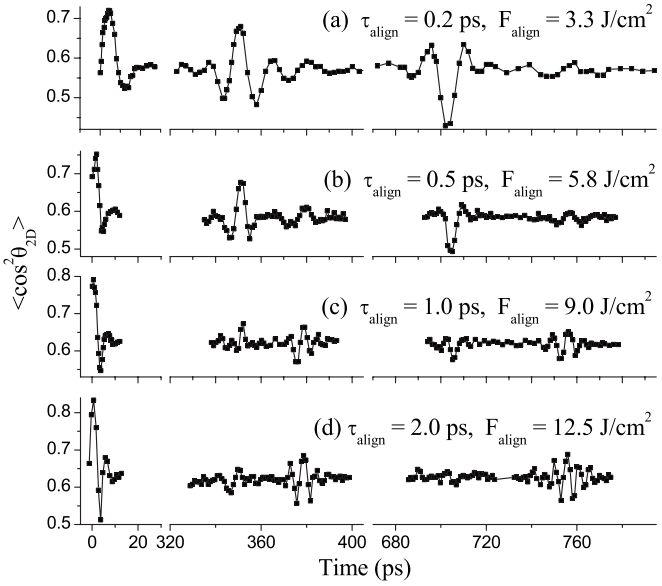

FIG. 3. $\langle\cos^2\theta_{2D}\rangle$ recorded in three time intervals representing the rotational dynamics shortly after the alignment pulse and in the two first regions with *J*-type and *C*-type revivals. The measurements are carried out at four different fluences and pulse durations, indicated on each panel. The peak intensities are (a) 1.6×10^{13}, (b) 1.1×10^{13}, (c) 8.5×10^{12}, and (d) 5.9×10^{12} W/cm^2. In the absence of the alignment pulse $\langle\cos^2\theta_{2D}\rangle$=0.5. Each data point is obtained from an I^+ image accumulated over 1500 laser shots and containing ~40 000 ion hits.

The angular information in the ion images is quantified by calculating $\langle\cos^2\theta_{2D}\rangle$, where θ_{2D} is the angle between the alignment pulse polarization and the projection of the ion velocity vector in the detector plane [18]. This is easily performed because the spatial coordinates of each I^+ ion hit on the detector are recorded. As noted in previous works [18] the two distinct radial rings observed in the ion images result from I^+ ions Coulomb fragmenting with either a $C_6H_5^+$ (innermost ring) or a $C_6H_5^{2+}$ (outermost ring) partner ion. The alignment dynamics presented in Fig. 3 are based on $\langle\cos^2\theta_{2D}\rangle$ values calculated only from ions detected in the radial range corresponding to the (I^+, $C_6H_5^{2+}$) channel. By doing so, we restrict the alignment intensities probed to a narrow range close to the maximum value, because the high nonlinearity of the multiphoton process leading to (I^+, $C_6H_5^{2+}$) formation occurs efficiently only in the spatial regions of the alignment laser beam near its focal point.

To appreciate the measure of alignment used in Fig. 3 we note that, with our experimental polarization geometry, where the probe pulse is polarized perpendicular to the detector plane and the alignment pulse is polarized parallel to the detector plane, $\langle\cos^2\theta_{2D}\rangle$ equals 0.5, 1, and 0 for randomly oriented, perfectly aligned, and perfectly anti-aligned molecules, respectively.

Figure 3 shows $\langle\cos^2\theta_{2D}\rangle$ in three selected time windows representing the intervals where the important alignment transients occur. The measurements are carried out for four different durations of the alignment pulse and, in each case, for an intensity adjusted to the largest value the molecules can tolerate without ionizing.[2] Shortly after the pulse a local maximum in the degree of alignment is observed for all the four different durations. The precise locations and amplitudes of these maxima are determined by the duration and the intensity of the alignment pulse [8]. In particular, it is seen that the peak value of the prompt alignment maximum increases and shifts to earlier times as the duration is increased. This is due to the higher fluence of the longer pulses and is in excellent agreement with our numerical results, as noted below.

Next, we focus on the alignment dynamics in the two time intervals where the rotational revivals occur. It is seen that varying the fluence (through the pulse duration) has a dramatic effect on the relative intensity of the revivals as well as on their internal structure. At the lowest fluence [Fig. 3(a)] a prominent maximum occurs at t=350.4 ps and similarly a prominent minimum at t=702.8 ps. Their locations and separation (352.4 ps) identify them as the half *J*-type and the full *J*-type revival, respectively. At F_{align}=5.8 J/cm^2 (τ_{align}=0.5 ps) the *J*-type revivals still dominate, although the transients are narrower than for F_{align}=3.3 J/cm^2, resulting from a broader rotational wave packet created by the higher fluence of the longer pulse. Also, weak maxima at t=379.7 and 756.8 ps are observed. Their positions as well as their separation (377.1 ps) identify them as the first and second *C*-type revivals, respectively.

When the fluence is increased to 9.0 J/cm^2 the amplitude and the modulation (i.e., the difference between the maximum and minimum value of $\langle\cos^2\theta_{2D}\rangle$) of the *J*-type revivals are reduced. By contrast, the amplitude and modulation of the *C*-type revivals increase and the revivals become more structured with several local maxima and minima. At F_{align} =12.5 J/cm^2 the oscillatory structure of the *C*-type revivals is significantly enhanced; in particular, the second *C*-type revival exhibits seven local maxima and minima. At the same time, the *J*-type revivals are suppressed so strongly that they are barely visible.

The quantum-mechanical oscillatory structure of Figs. 1 and 3 has been observed numerically in our previous work on the alignment dynamics of asymmetric top molecules, and is well understood theoretically [2,15]. Earlier studies, however, did not observe this structure experimentally, due to the combination of Boltzmann averaging over a dense thermally populated rotational ensemble and spatial averaging over the intensity distribution of the alignment pulse. Both averaging procedures were numerically shown to wash out much of the information contained in the revival structure. The current low rotational temperature and small ratio of the probe and alignment beam spot sizes introduce a new opportunity for extracting the physical content of our observations by comparison with the numerical results.

Figure 4 shows numerical calculations of the iodobenzene rotational revivals at four different fluences (pulse durations)

[2]For τ_{align}=2.0 ps the available laser power was not quite high enough to reach this limit. We estimate that the intensity could be increased by 20–30 % without causing ionization. This might slightly increase the modulation and number of oscillations in the *C*-type revivals.

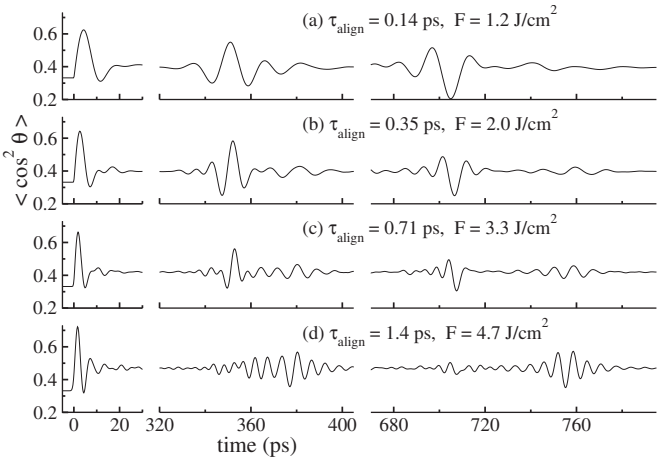

FIG. 4. Computed revival spectra of iodobenzene immediately after the alignment pulse and in the vicinity of the first and second revivals at four different fluences and durations (indicated on each panel). $T_{\mathrm{rot}}=1.0$ K and the peak intensities are (a) 8.0×10^{12}, (b) 5.5×10^{12}, (c) 4.4×10^{12}, and (d) 3.1×10^{12} W/cm^2.

of the alignment pulse. It should be clear that quantitative comparison of the experimental and numerical results is not our goal—indeed, the measured and computed observables ($\langle\cos^2\theta_{2D}\rangle$ and $\langle\cos^2\theta\rangle$, respectively) are rather different. The gratifying agreement of Figs. 3 and 4, however, substantiates our confidence in the message of Fig. 1 and in the ability of experiments to record the information-rich, low-temperature rotational revivals in complex molecules.

In summary, we showed that the nonadiabatic alignment dynamics of asymmetric top molecules can be controlled by the fluence of the alignment pulse. When the laser fluence is increased, the quasiperiodic or nonperiodic rotational revivals of an asymmetric top molecule approach a simple, periodic rotation that characterizes a single axis. A more complete orientational control requires confinement of all three molecular axes to given space-fixed axes. Recently, it was suggested that such (field-free) three-dimensional alignment can be obtained by sequences of short pulses with timings matching rotational periods [12]. We believe that understanding and controlling rotational dynamics, as demonstrated here, is a necessary requirement for exploiting wave-packet technology to achieve efficient three-dimensional alignment.

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