

Climbing the Rotational Ladder to Chirality

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Molecular chirality is conventionally understood as space-inversion-symmetry breaking in the equilibrium structure of molecules. Less well known is that achiral molecules can be made chiral through extreme rotational excitation. Here, we theoretically demonstrate a clear strategy for generating rotationally induced chirality: An optical centrifuge rotationally excites the phosphine molecule (PH_3) into chiral cluster states that correspond to clockwise (R enantiomer) or anticlockwise (L enantiomer) rotation about axes almost coinciding with single P–H bonds. The application of a strong dc electric field during the centrifuge pulse favors the production of one rotating enantiomeric form over the other, creating dynamically chiral molecules with *permanently* oriented rotational angular momentum. This essential step toward characterizing rotationally induced chirality promises a fresh perspective on chirality as a fundamental aspect of nature.

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Chiral molecules exist in two structural forms known as enantiomers, which are the mirror image of each other and thus nonsuperimposable by translation and rotation. The wave functions of the enantiomers have no definite parity, i.e., space-inversion symmetry, as they tunnel periodically from one structure to the other on a timescale determined by the energy barrier separating the two enantiomeric forms. Molecular chirality, in the traditional sense, is associated with the barriers formed by the static potential energy surface, typically so large that the enantiomers do not readily interconvert at room temperature and can be separated by chemical means and stored. There is, however, the possibility to induce and control chirality in achiral molecules through extreme rotational excitation into states where centrifugal distortions produce equivalent asymmetric structures separated by high kinetic energy barriers [1]. The appearance of such chiral high angular momentum states is closely linked to the energetic clustering of rotational states, an effect displayed by certain polyatomic molecules exhibiting local mode vibrations [2]. Given the importance of chirality to our understanding of molecular and material behavior, the ability to create chirality in achiral systems is of great fundamental interest. For example, it has recently been shown that isotopic substitution can induce chirality in achiral molecules and catalyze asymmetric reactions [3,4].

Very little is known about the phenomenon of rotationally induced chirality (RIC), but ultrashort-pulse strong-field laser physics has brought new impetus to the preparation of molecules in highly excited rotational states. The main obstacle to overcome when generating large amounts

of rotational excitation is that selection rules permit only small changes in the overall angular momentum J . With the development of clever adiabatic and nonadiabatic approaches [5,6], this is now far less challenging and it is possible to efficiently create rotational wave packets with a narrow and well-defined distribution of states. Molecular superrotors, as they are known in the literature, display novel behavior. For example, they are far more resistant to collisions and reorientation [7–9] making them interesting objects for scattering [10], spectroscopy [11], and dynamics [12]. Superrotors provide an ideal testing ground for exploring RIC, and by learning to control and characterize this dynamic effect, e.g., the optical activity, there is an opportunity to gain new insights into chirality, specifically motion-dependent chiral systems and the nature of their interactions.

In this Letter, a clear strategy for producing dynamically chiral molecules through extreme rotational excitation is presented. The scheme is outlined in Fig. 1 and realized through robust quantum mechanical simulations of RIC in the phosphine molecule (PH_3). PH_3 is initially considered

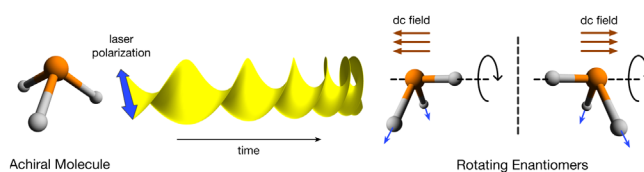


FIG. 1. Rotationally induced chirality in PH_3 using an optical centrifuge in conjunction with a static electric field. Reversing the direction of the dc field produces the other rotating enantiomer.

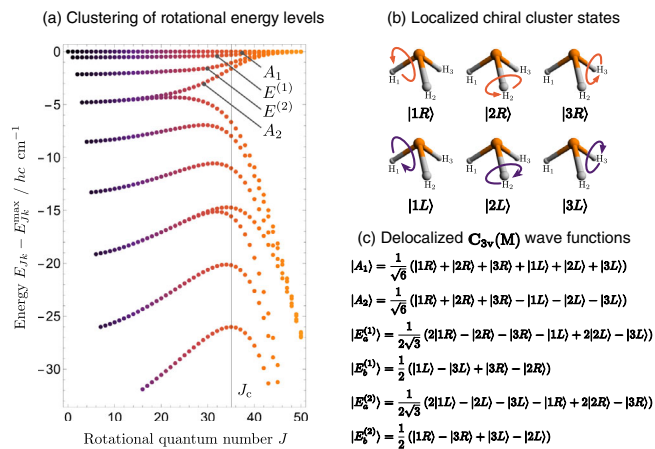


FIG. 2. Rotational energy level clustering in the ground vibrational state of PH_3 , c. f. Fig. 2 of Ref. [14]. (a) The energy difference $E_{Jk} - E_{Jk}^{\max}$ was plotted for each rotational energy level E_{Jk} relative to the maximum energy E_{Jk}^{\max} in its J multiplet. (b) Schematic representation of the localized chiral cluster states, which are separated by high kinetic energy barriers. (c) Wave functions of the delocalized rotational cluster states in the representation of the localized chiral cluster states.

in its ground rovibronic state as a symmetric top molecule possessing $C_{3v}(M)$ molecular symmetry; inversion tunneling has a high barrier and is neglected. An optical centrifuge [13], which is a nonresonant, linearly polarized laser pulse that undergoes accelerated rotation about the direction of propagation, is used to adiabatically spin phosphine into highly excited rotational states. Above the critical value of $J_c \approx 35$, the rovibrational energy levels of PH_3 form sixfold degenerate clusters [14], which classically can be interpreted as a “racemic mixture” of clockwise (R) and anticlockwise (L) rotations about localization axes approximately coinciding with a P–H bond, see Fig. 2. Because of strong centrifugal coupling, three dynamic and symmetrically equivalent molecular structures emerge, where one of the P–H bonds about which the molecule rotates, is shorter than the other two. The three asymmetrical structures can rotate in either a clockwise or anticlockwise direction. They are energetically indistinguishable from one another and separated by high kinetic energy barriers, which is analogous to conventional “static” enantiomers with potential barriers. If PH_3 is prepared in a state corresponding to a preferred direction of rotation in the laboratory frame, the permutation symmetry is broken by centrifugal distortions, while parity is broken by unidirectional rotation. The result is a rotating enantiomer, where clockwise rotation corresponds to the R enantiomer, and anticlockwise rotation to the L enantiomer.

The relationship between the localized chiral cluster states and the delocalized wave functions in the $C_{3v}(M)$ symmetry group is shown in Fig. 2. It is evident that any interaction of the permanent molecular electric dipole moment with a strong electric field will mix the delocalized

wave functions of quasidegenerate states, e.g., A_1 with A_2 , in such a way that combinations of states dominated by either R or L localized states are generated. Hence, by applying a strong dc field during the centrifuge pulse either one of the rotating enantiomers can be exclusively produced depending on the direction of the field. This is an essential step toward characterizing RIC as each enantiomer can be isolated for further investigation. Furthermore, it demonstrates that an ensemble of dynamically chiral molecules with “permanently” oriented rotational angular momentum can be created, where the orientation of the angular momentum with respect to the P–H bond, about which rotation takes place, defines the rotating enantiomer. That is, the difference between the centrifuge with and without the dc field is the orientation of the angular momentum in the molecular frame.

It should be noted that the Raman-type excitation by the optical centrifuge couples states with the same symmetry, whereas the dc field couples states whose product-symmetry spans the symmetry of the dipole moment A_2 , i.e., $A_1 \leftrightarrow A_2$ and $E \leftrightarrow E$. Therefore, depending on the symmetry of the initial rotational state, only a pair of A_1 and A_2 or a pair of $E^{(1)}$ and $E^{(2)}$ delocalized components of the rotational cluster will give rise to the effect of RIC.

The theoretical approach is described in detail in the Supplemental Material [15]. Numerical simulations were fully quantum mechanical and considered all major ground-state electronic correlation within the Born-Oppenheimer approximation, nuclear motion, and external field effects to an accuracy capable of supporting high-resolution spectroscopic measurements, i.e., sub-cm^{-1} accuracy for vibrational and 10^{-4} – 10^{-5} cm^{-1} for rotational energies. The stationary rovibrational energies and eigenfunctions of PH_3 up to $J = 60$ were computed by direct numerical variational calculations [23–25] from an empirically refined, six-dimensional potential energy surface [26]. To describe external field effects, the matrix elements of the electric dipole moment and electric polarizability tensor were evaluated in the basis of rovibrational states. In quantum dynamics simulations, which employed the computer program RICHMOL [27], the time-dependent wave function was built from a superposition of rovibrational eigenfunctions with the time-dependent coefficients obtained by numerical solution of the time-dependent Schrödinger equation using the split-operator method.

An optical centrifuge with maximum intensity $\epsilon_0 = 5.2 \times 10^{13} \text{ W/cm}^2$ and chirp rate $\beta = (2\pi c)^2 25 \text{ cm}^{-2}$ was applied along the laboratory-fixed Z axis for a duration of $t = 36.8 \text{ ps}$. Simulations were started in the rovibrational ground state ($J = k = m = 0$), corresponding to samples that can be produced from cold beams using the electric deflector [28,29]. The centrifuge field aligns the most polarizable molecular axis through the interaction with the induced molecular dipole moment, trapping and forcing the molecule to follow the rotating polarization.

PH_3 is predominantly excited via $\Delta J = 2$, $\Delta m = -2$ rotational Raman transitions through the highest energy state of each J value. Here, the quantum numbers k and m correspond to the projection, in units of \hbar , of J onto the molecule-fixed z axis and laboratory-fixed Z axis, respectively. For calculations involving a static electric field, a field strength of 1 MV/cm [30] was applied along the laboratory-fixed Z axis.

The phenomenon of RIC is well illustrated with the chosen laser parameters, but the centrifuge intensity ϵ_0 is expected to cause ionization of PH_3 . However, the same conclusions can still be reached with lower optical and static field strengths, and when using an experimentally realistic pulse envelope for the optical centrifuge, see the Supplemental Material [15]. It should be noted that because PH_3 is highly toxic, we anticipate that future experiments will be performed on other systems, most likely heavier rotors, which require weaker optical and static field strengths, allowing for the practical realization of this proposal.

In Fig. 3, the wave packet population at the end of the centrifuge pulse is plotted along with the rotational probability density function $P(\theta, \chi) = \int dV d\phi \psi(t)^* \psi(t) \sin \theta$, which illustrates the orientation of the molecule relative to the possible axes of rotation. Here, θ, χ, ϕ denote the Euler angles, dV is the volume element associated with the vibrational coordinates, and $\psi(t)$ is the wave packet. The dominant contribution of $\sim 25\%$ to the wave packet is from the $J = 42, m = -42$ energy level of the top cluster state at 7686 cm^{-1} . In PH_3 , clustering occurs above $J_c \approx 35$ and is related to the six islands that emerge on the rotational density plot seen in Fig. 3(a), which correspond to clockwise ($\theta < \pi/2$) and anticlockwise ($\theta > \pi/2$) rotation about an axis almost coinciding with one of the P–H bonds. Application of a strong dc field in the $-Z$ or $+Z$ direction for the duration of the centrifuge pulse, shown in Fig. 3(b), produces only clockwise (R) or anticlockwise (L) rotating enantiomers, respectively. This is a result of the brute-force orientation of the permanent dipole moment at the time

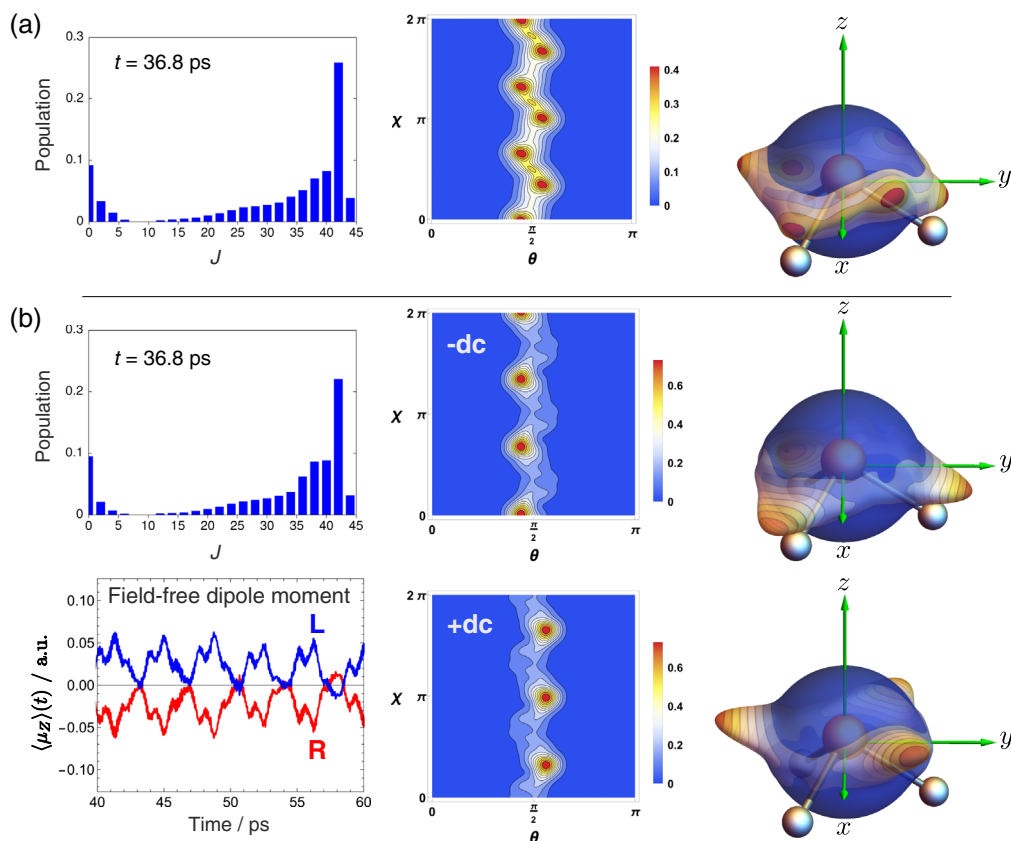


FIG. 3. Wave packet population by $m = -J$ stationary states and rotational probability density function $P(\theta, \chi)$, in terms of the Euler angles θ and χ , at the end of the centrifuge pulse ($t = 36.8$ ps), (a) without, and (b) with a dc field of ± 1 MV/cm applied. Wave packet population of stationary states with odd J quantum numbers or $m \neq -J$ are much smaller and not shown in the plot. The two-dimensional rotational density contour plot, shown in the middle, has been projected onto a sphere, shown on the right hand side, to illustrate the orientation of PH_3 and the molecular frame relative to the rotation axes. Each high-density island (red) indicates an axis of rotation and x, y, z refer to the molecule-fixed axis system. In the bottom left hand corner, the time evolution of the expectation value of the laboratory-fixed effective dipole moment $\langle \mu_z \rangle$ has been calculated for the R and L rotating enantiomers. The exhibited antiphase behavior between the rotating enantiomers confirms chirality.

when population is transferred into the cluster states. A detailed analysis of the effect of the dc field shows that, in principle, the field is only necessary during the time when the cluster states are populated, whereas it is a loss channel at the start of the centrifuge, and it does not affect the dynamics once the population is within a well-defined angular momentum enantiomer. In order for the population to be adiabatically transferred from the quasi-free-rotor state to the mixed-parity “single-enantiomer” cluster state, the dc field splitting must be large in comparison to the traversal time of the J manifold by the centrifuge. Classically speaking, the dc field has to be strong enough to favor one enantiomer over the other when the dipole moment is still nearly perpendicular to the dc field.

This mixed-field enantiomer selectivity allows us to probe the chirality of the R and L enantiomers by measuring, for instance, the free-induction decay [31,32] by a phase-locked microwave receiver [33], see also further details in the Supplemental Material [15]. As expected, the time evolution of the permanent electric dipole moment expectation value $\langle \mu_z \rangle$ in the laboratory-fixed frame shows antiphase behavior between the rotating enantiomers.

If PH_3 is excited above $J = 42$, the axis of rotation moves closer to the P–H bond [14]. However, our simulations have shown that it is difficult to efficiently transfer population to higher J states, notably across the range $J \approx 40$ –50. Instead, wave packet population gradually spreads across several energy levels and cluster states at each excitation of J , resulting in a spectrally broadened rotational wave packet. For example, if the centrifuge pulse used in this work is left to propagate until $t = 48.5$ ps, only 1% of the population is transferred to the $J = 58$, $m = -58$ energy level of the top cluster state at $14\,133\text{ cm}^{-1}$. Clustering represents a significant change in the rotational dynamics and as PH_3 rotates faster its structure distorts, leading to the breakdown of $C_{3v}(M)$ molecular symmetry. The quantum number k is no longer a good quantum number and the $\Delta k = 0$ selection rule that partially governed transitions up to J_c becomes weak. The spreading of the wave packet population can be marginally counteracted with a more tailored centrifuge pulse [34], e.g., nonlinear angular acceleration and intensity chirping; however, for the purpose of this study it is enough to show that PH_3 is indeed chiral when excited to the $J = 42$, $m = -42$ cluster state.

The concept of true and false chirality was introduced to clarify situations where motion played an essential role [35]. Truly chiral systems possess two distinct enantiomeric states that can be interconverted by space inversion, but not by time reversal combined with any proper spatial rotation. As shown in Fig. 4, if PH_3 can be forced to translate along the axis of rotation then the system is truly chiral, i.e., exhibits time-invariant enantiomorphism. If not, the system possesses false chirality, i.e., time-noninvariant

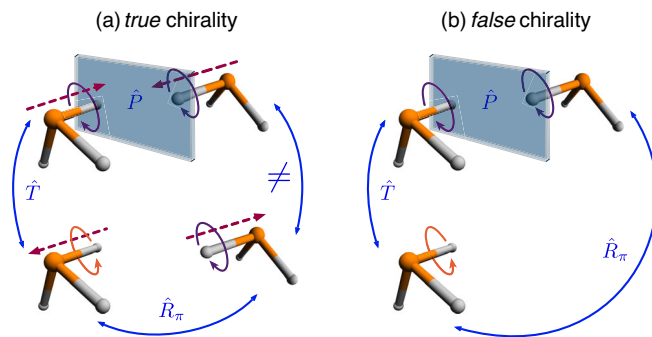


FIG. 4. Definition of true and false chirality. (a) If PH_3 is translating along the axis of rotation (dashed arrow), space inversion (\hat{P}) is not equivalent to time reversal (\hat{T}) combined with any proper spatial rotation (\hat{R}_π) and the system is truly chiral. (b) If PH_3 is not translating, the system exhibits false chirality as space inversion is equivalent to time reversal combined with spatial rotation.

enantiomorphism. Distinguishing between true and false chirality has implications for topics such as parity violation [36] and absolute enantioselection [37], and there is still a great deal to learn about this distinction. For example, it was recently reported that a falsely chiral influence can generate an enantiomeric excess in a reaction far from equilibrium [38]. In PH_3 there is an opportunity to further explore the differences between true and false chirality by probing the system with and without translation, or by studying isotopically substituted species such as PHD_2 , which will possess truly chiral cluster states even when it is not translating along the axis of rotation.

To establish how, if at all, RIC differs from traditional static chirality, it will be necessary to study the interaction of the rotating enantiomers with other chiral entities such as light. Achieving a deeper understanding should contribute to the development of chirality-based molecular and material properties, new states of matter, and the potential utilization of RIC in novel metamaterials or optical devices. It is also of interest to image RIC using sensitive techniques such as photoelectron circular dichroism (PECD) [39]. It has been shown that changes in the nuclear geometry caused by vibrational motion can reverse the forward-backward asymmetry in the photoelectron angular distribution [40]. One can, therefore, expect that PECD measurements of RIC may reveal unexpected behavior. We plan to investigate these topics in future work.

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