

Nuclear spin symmetry breaking and spin polarization in rotational energy level clusters

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We present the first quantum mechanical study of hyperfine effects in the rotational cluster states of a symmetric triatomic molecule H_2S . Rotational clusters arise from spontaneous symmetry breaking induced by high-angular-momentum rotational motions in certain rigid molecules, resulting in dynamic enantiomorphism driven by kinetic distortion effects. Hyperfine interactions in the cluster states lead to collision-free breaking of nuclear spin symmetry, with the magnitude of nuclear spin *ortho-para* mixing significantly exceeding that in other states with same or lower angular momentum. The *ortho-para* mixing induces nuclear spin polarization in the laboratory frame and gives rise to two sets of enantiomers, which have different energies and oppositely oriented nuclear spin projections. Although hyperfine interactions preserve parity, they lift the degeneracy of opposite-parity cluster states. This phenomenon, previously observed experimentally, is explained as a result of tunneling between rotating enantiomers, facilitated by the Pauli exclusion principle.

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Introduction. Chirality, in its traditional sense, refers to the time-invariant property of certain molecules to exist in two nearly energetically equivalent configurations, known as enantiomers, which are nonsuperimposable mirror images of each other. This means that enantiomers cannot be brought into coincidence through spatial rotations or translations. The concept of chirality has been broadened to include time-noninvariant enantiomorphism, named “false chirality,” which extends the original notion by adding time reversal as the operation that interconverts the enantiomers [1–3]. Falsely chiral influences, such as the interaction of chiral molecules with magnetic fields [4–6] or chiral electric fields [7–9], can distinguish between enantiomers, however, only in processes that either are prevented from reaching equilibrium or have not yet reached it [10,11].

Much like the potential energy surface (PES) of a statically chiral molecule has two equivalent minima corresponding to molecular structures related by parity inversion, kinetic energy can similarly localize molecular motions into two parity-related configurations, making a statically achiral molecule dynamically chiral. This form of dynamic chirality can arise from kinetic effects such as centrifugal distortion and Coriolis coupling, that is, under nonequilibrium conditions, and falls into the category of false chirality.

A notable example is the rotational energy level clustering effect [12–14], where the rovibrational motions of a nonchiral molecule become localized around several stable axes of rotation in the molecular frame. These axes are separated by high kinetic energy barriers, leading to a symmetry breaking of the molecule [15]. Other examples of kinetic effects include the dynamical symmetry breaking in structural transitions of atomic clusters [16], chirality-dependent coupling of molecular rotation and translation in mixtures [17], and the transfer of macroscopic chirality in fluid and mass transport in helical devices [18].

The phenomenon of rotational energy level clustering occurs in molecules exhibiting local mode behavior [19], where molecular bonds are nearly orthogonal to each other such that the rotation of the molecule remains largely unaffected by Coriolis-type interactions with vibrational modes [14]. This effect has been investigated extensively in quantum and semiclassical calculations for symmetric triatomic XH_2 -type molecules (e.g., $X = \text{S}$ [20,21], P [22,23], Si [24], Po [25], Te [26,27], Se [28]) and tetraatomic XH_3 -type molecules (e.g., $X = \text{P}$, Bi , Sb) [29], their deuterated isotopologues [30], and for SO_3 [31] and PF_3 [32]. Experimentally, rotational clusters were observed in H_2Se [33,34] and dimethyl sulfoxide [35,36]. Additionally, several experimental studies reported effects associated with the localization of the rotational axis in the molecular frame, including observations of nonergodic transitions in fullerene C_{60} [37] and hyperfine-induced lifting of parity degeneracy in SF_6 [38], PH_3 [39], and SiF_4 [40].

Previous theoretical studies of molecules with localized rotations were primarily focused on characterizing their energy levels and spectroscopic transitions. In this work, we extend these studies by investigating the effects of nuclear spin hyperfine interactions in rotational cluster states, using first-principles calculations for the H_2S molecule. Our

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results reveal that hyperfine interactions break nuclear spin symmetry, resulting in nearly equal mixing of *ortho* and *para* nuclear spin states of the hydrogen atoms, with energy splittings on the order of MHz. These represent the largest *ortho-para* splittings predicted for similar hydride molecules, for example, water [41]. The *ortho-para* coupling induces strong polarization of nuclear spins along the axis of rotation, with opposite spin orientations in the hyperfine-split state components. To our knowledge, this presents the first direct theoretical evidence of a connection between nuclear spin symmetry breaking and induced chirality. This phenomenon is similar to the Rashba effect, where the electron spin-orbit coupling arises due to inversion symmetry breaking [42,43], as well as to the related electronic chirality-induced spin selectivity effect, which currently remains only partially understood [4,6].

Additionally, we predicted the hyperfine-induced lifting of degeneracy in states of opposite parity, a phenomenon previously observed in SF₆, PH₃, and SF₄ molecules [38–40], which, like H₂S, exhibit rotational level clustering. These observations provide direct experimental evidence supporting our theoretical predictions. The mechanism behind the degeneracy lifting is explained by the interplay between tunneling between rotating enantiomers and nuclear spin polarization, governed by the Pauli exclusion principle.

We performed high-accuracy variational calculations of rovibrational states and hyperfine interactions in H₂S, employing the exact rovibrational kinetic energy operator and a high-accuracy spectroscopically refined PES [44]. Details of the vibrational coordinates, basis set, hyperfine interaction, and variational solution are provided in the Supplemental Material [45]. The electronic structure calculations of hyperfine spin-rotation tensor employed all-electron CCSD(T) method, as implemented in the quantum chemistry package cfour [46–49], with the augmented core-valence correlation-consistent basis sets aug-cc-pwCVTZ [50] for sulfur and aug-cc-pVTZ [51,52] for hydrogen atoms. A complete documented Python implementation of all calculation steps is available in a public repository [53].

An effective way to visualize rotational cluster states is by plotting rotational energies for different total angular momentum quantum numbers J , with energies shifted relative to the highest energy within a given multiplet, as shown in Fig. 1(a). A distinct characteristic of rotational cluster states is the localization of the rotational axis along the S–H bonds, which enables their clear identification. This property is manifested in the reduced rotational probability density, as a function of two Euler angles $\rho(\theta, \chi) = \int |\Psi|^2 dq_1 dq_2 \dots dq_{3N-6} d\phi \sin\theta$, where the integration averages over all vibrational modes ($q_1, q_2, \dots, q_{3N-6}$) and the rotation (ϕ) around the laboratory Z axis. In Fig. 1(b), the normalized densities $\rho(\theta, \chi)$, plotted on a unit sphere, illustrate the distribution of the rotational axis in the molecular frame for three groups of cluster states. The maxima in the plots correspond to localized rotations about axes closely aligned with the S–H bonds, with two oppositely located maxima along each bond corresponding to left- and right-handed rotations.

The chirality of cluster states emerges as a result of breaking of parity (and time) reversal symmetry, combined with the permutational isolation of the two identical hydrogen

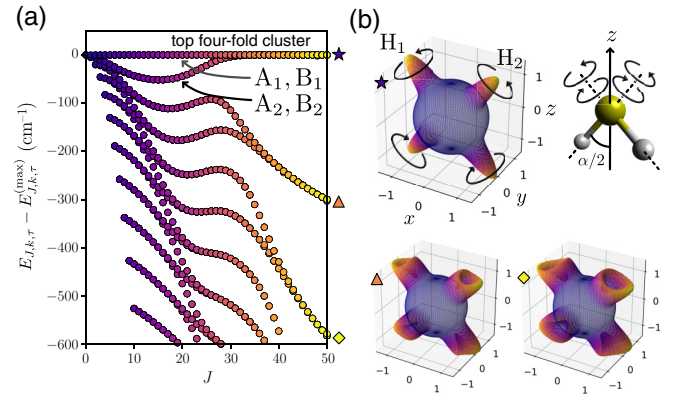


FIG. 1. Rotational energy level clustering in the ground vibrational state of H₂S. (a) Energy differences $E_{J,k,\tau} - E_{J,k,\tau}^{(\max)}$ (cm^{−1}) plotted for each rotational energy level $E_{J,k,\tau}$ relative to the maximum energy $E_{J,k,\tau}^{(\max)}$ within its J multiplet. The rotational states group into clusters of four, corresponding to the A₁, A₂, B₁, and B₂ symmetries in C_{2v}. (b) Reduced rotational probability density distributions of the rotational axis in the molecular frame for three groups of cluster states at $J = 50$ and $|m| = J$. The molecular-frame z axis is defined to bisect the $\angle\text{H}_1\text{--S--H}_2$ valence angle. The four maxima correspond to left- or right-handed rotation about axes closely aligned with the S–H₁ or S–H₂ bond.

nuclei. Tunneling between enantiomers is suppressed by high kinetic energy barriers when the molecule is in a high angular momentum state. The four cluster states of a triatomic C_{2v}-symmetry molecule, characterized by A₁, A₂, B₁, and B₂ symmetries, correspond to racemic mixtures of the four rotating enantiomers L₁, R₁, L₂, and R₂, representing left- (L) and right-handed (R) rotations about the S–H₁ or S–H₂ bond:

$$\begin{aligned} |A_1\rangle &= [(R_1 + R_2) + (L_1 + L_2)]/2, \\ |A_2\rangle &= [(R_1 + R_2) - (L_1 + L_2)]/2, \\ |B_1\rangle &= [(R_1 - R_2) - (L_1 - L_2)]/2, \\ |B_2\rangle &= [(R_1 - R_2) + (L_1 - L_2)]/2. \end{aligned} \quad (1)$$

By fixing the direction of rotation in the laboratory frame, the rotating enantiomers correspond to opposite orientations of one of the S–H bonds along the rotational axis, as illustrated in Fig. 2(a). The excitation of unidirectional rotation can be achieved using an optical centrifuge [54,55], which

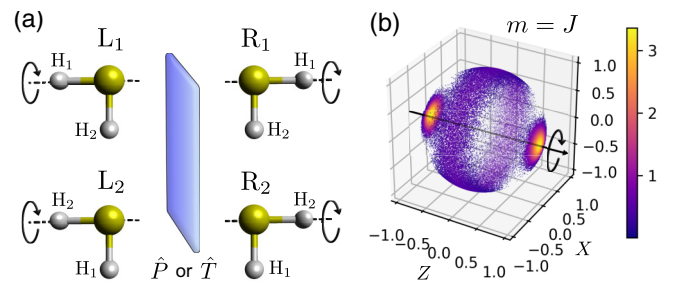


FIG. 2. (a) Classical representation of rotating enantiomers in the cluster states of H₂S. (b) Probability distribution of hydrogen nuclei in the laboratory frame, plotted in Cartesian coordinates on a unit sphere, for a selected cluster state of H₂S at $J = 50$ and $m = J$.

was also demonstrated for rotational cluster states [21,23,56]. Figure 2(b) shows the probability distribution of hydrogen nuclei in the laboratory frame, plotted on a unit sphere for a cluster state at $J = 50$ and $m = J$. The distribution illustrates the spatial isolation of the two hydrogen nuclei: one is located at the poles of the sphere, while the other is distributed along a ring, representing a superposition of two classical left- and right-handed rotations about an axis closely aligned with one of the S–H bonds. Tunneling between enantiomers associated with rotation about the same bond, i.e., $L_1 \rightarrow R_1$ and $L_2 \rightarrow R_2$, requires reversing the direction of rotation, which is energetically unfavorable. However, since the two hydrogen atoms are identical, an alternative pathway $L_1 \rightarrow R_2$ and $L_2 \rightarrow R_1$ exists, which is more energetically feasible. This transition can be achieved through a rotation of the molecule by about 90° around an axis perpendicular to the main rotational axis.

An additional symmetry-breaking effect arises in rotational cluster states due to differences in the internal magnetic field environments experienced by the two identical hydrogen nuclei, which rotate on distinctly different orbits. The interaction of magnetic field, induced by molecular rotation, with the nuclear spins $I = 1/2$ of the hydrogen nuclei (sulfur ^{32}S has spin zero) is described by the spin-rotation coupling. We neglect the spin dipole-dipole interaction, which is typically weaker and does not contribute to nuclear spin symmetry breaking in triatomic molecules [41]. The total spin-rovibrational wave functions $|F, m_F\rangle$ are built as symmetry-adapted combinations of the coupled products of rovibrational wave functions $|J, m_J\rangle$ and nuclear spin functions, *para* $|I = 0, m_I\rangle$ and *ortho* $|I = 1, m_I\rangle$. Here, J , I , and F are the quantum numbers of rotational, total nuclear spin, and total angular momentum operators, respectively, with m_J , m_I , and m_F denoting their corresponding projections on the laboratory Z axis.

The symmetrization postulate requires the total wave function of the H_2S molecule to change sign upon exchange of the hydrogen nuclei, meaning that it must transform as one of the irreducible representations B_1 or B_2 of the C_{2v} symmetry group. Accordingly, the *ortho* spin state $|I = 1\rangle$ of A_1 symmetry can form a symmetry-allowed product with the rovibrational states of B_1 and B_2 symmetries. Similarly, the *para* spin state $|I = 0\rangle$ of B_2 symmetry can form a product with the rovibrational states of A_1 and A_2 symmetries. The energy level diagram in Fig. 3(a) illustrates this coupling of rotational angular momentum with nuclear spin for the four cluster states. In the absence of hyperfine interactions, the cluster states consist of two pairs of nearly exactly degenerate states of opposite parity, corresponding to rovibrational symmetries A_1 and B_1 , as well as B_2 and A_2 . This near-degeneracy arises even at modest rotational excitations due to close proximity of the H_2S molecule to a near-oblate symmetric top.

The hyperfine interactions couple states of the same parity but with different total nuclear spin, i.e., $|A_1, J\rangle|I = 0\rangle$ with $|B_2, J\rangle|I = 1\rangle$ and $|B_1, J\rangle|I = 1\rangle$ with $|A_2, J\rangle|I = 0\rangle$. As a result, states of the same parity split, breaking the nuclear spin symmetry with nearly equal mixing of *ortho* and *para* components. The corresponding contributions to splittings increase from 514 kHz at $J = 50$ to 2.2 MHz at $J = 60$, whereas the base splittings between same-parity cluster states (i.e., without considering hyperfine interactions) decrease from

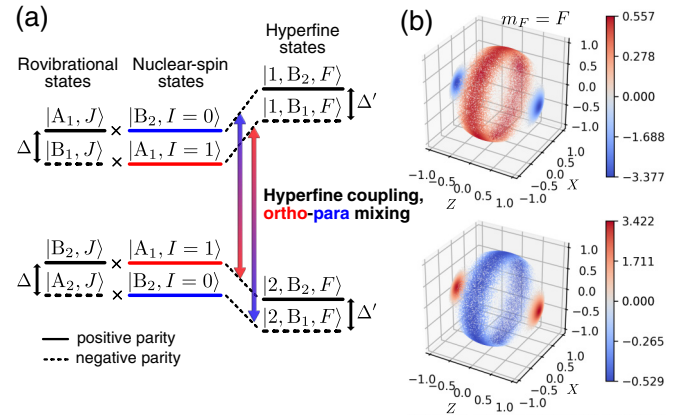


FIG. 3. (a) Energy level diagram of H_2S , illustrating the coupling of rotational cluster states with *para* ($I = 0$) and *ortho* ($I = 1$) nuclear spin states of the hydrogen atoms. Hyperfine interactions break spin symmetry, splitting states of the same parity and also lifting the original degeneracy ($\Delta \approx 0$) between opposite-parity states ($\Delta' > 0$). (b) This interaction polarizes the nuclear spins, resulting in opposite spin orientations along the rotational axis for states of the same parity, as illustrated by the computed spin-density distributions in the laboratory frame.

3.1 MHz at $J = 50$ down to 1.5 kHz at $J = 60$. Analysis of spin-rotation coupling matrix elements reveals that cluster states exhibit significantly larger coupling elements compared to other states. Interestingly, cluster states also appear in vibrationally excited states, with the spin-rotation coupling matrix elements of comparable magnitude to those in the ground-state cluster states, resulting in similarly strong *ortho-para* mixing. Rotational density plots for these states, along with a table of hyperfine coupling matrix elements, energies, splittings, and mixing coefficients, are provided in the Supplemental Material [45].

The breaking of nuclear spin symmetry induces spin polarization, with nuclear spin projections oriented along the rotational axis in the opposite directions for the two split energy bands. Figure 3(b) illustrates this, showing calculated spin densities of hydrogen nuclei in the laboratory frame, plotted in Cartesian coordinates on a unit sphere. The spin densities are calculated as $\rho_l(\mathbf{r}) = \sum_{i=1}^2 \langle l, B_1, F | \delta(\mathbf{r}_{H_i} - \mathbf{r}) \hat{\mathbf{I}}_{H_i} | l, B_1, F \rangle$, for two ($l = 1, 2$) hyperfine cluster states of B_1 symmetry and $m_F = F$, corresponding to unidirectional rotation of the molecule about the laboratory Z axis. The spin density has only a nonzero projection along the rotational axis. Notably, the spin-polarization vectors show opposite orientations for the hydrogen nucleus in the rotating bond and the hydrogen nucleus in the S–H bond about which the molecule rotates.

We analyze the effect of hyperfine coupling in terms of localized states representing rotating enantiomers. The relationship between rotating enantiomers and symmetry-adapted delocalized cluster states is given in Eq. (1). Each cluster state has a well-defined parity and is associated with either an *ortho* or *para* component of the total nuclear spin. Hyperfine interactions preserve parity but couple states with different spin components, resulting in the following linear combinations of

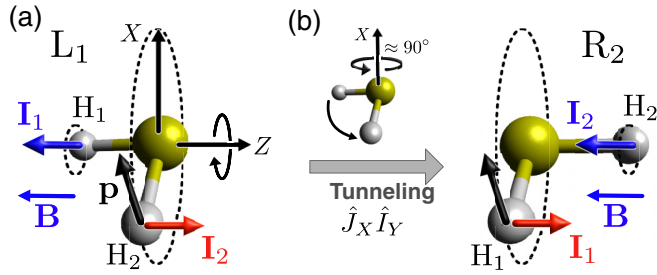


FIG. 4. (a) A schematic, classical depiction of the internally induced magnetic field generated by the localized rotation of H_2 about S- H_1 bond in L_1 rotating enantiomer of H_2S . The magnetic field polarizes the nuclear spin of H_1 . Due to nonoverlapping spatial distributions of the H_1 and H_2 nuclei, the Pauli exclusion principle requires the spin of H_2 to be polarized in the opposite direction of H_1 to maintain overall antisymmetry. (b) The energetically most feasible tunneling pathway between two rotating enantiomers involves a rotation of approximately 90° around an axis perpendicular to the main rotation axis, converting L_1 into R_2 and exchanging the spins of H_1 and H_2 .

rotating enantiomers:

$$\begin{aligned}
 |1, B_2\rangle &= (L_1 + R_1)|\uparrow\rangle|\downarrow\rangle + (L_2 + R_2)|\downarrow\rangle|\uparrow\rangle, \\
 |1, B_1\rangle &= (L_1 - R_1)|\uparrow\rangle|\downarrow\rangle + (L_2 - R_2)|\downarrow\rangle|\uparrow\rangle, \\
 |2, B_2\rangle &= (L_1 + R_1)|\downarrow\rangle|\uparrow\rangle + (L_2 + R_2)|\uparrow\rangle|\downarrow\rangle, \\
 |2, B_1\rangle &= (L_1 - R_1)|\downarrow\rangle|\uparrow\rangle + (L_2 - R_2)|\uparrow\rangle|\downarrow\rangle. \quad (2)
 \end{aligned}$$

Here, $|\uparrow\rangle|\downarrow\rangle$ and $|\downarrow\rangle|\uparrow\rangle$ represent the products of spin states of individual hydrogen nuclei, $|I_1, m_{I_1}\rangle|I_2, m_{I_2}\rangle = |\frac{1}{2}, \frac{1}{2}\rangle|\frac{1}{2}, -\frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle|\frac{1}{2}, \frac{1}{2}\rangle$, respectively. These states arise from symmetric and antisymmetric combinations of *para* ($|I, m_I\rangle = |0, 0\rangle$) and *ortho* ($|I, m_I\rangle = |1, 0\rangle$) total-spin states produced by hyperfine interactions [see diagram in Fig. 3(a)]. Specifically, the sum and difference of *para* and *ortho* states yield $|0, 0\rangle + |1, 0\rangle = \sqrt{2}|\frac{1}{2}, \frac{1}{2}\rangle|\frac{1}{2}, -\frac{1}{2}\rangle$ and $|0, 0\rangle - |1, 0\rangle = -\sqrt{2}|\frac{1}{2}, -\frac{1}{2}\rangle|\frac{1}{2}, \frac{1}{2}\rangle$. The expressions in Eq. (2) illustrate the spin polarization of the two hydrogen nuclei, with opposite nuclear spin projections along the axis of rotation. States with the same parity, such as $|1, B_2\rangle$ and $|2, B_2\rangle$, or $|1, B_1\rangle$ and $|2, B_1\rangle$, also have different relative orientations of the nuclear spins, which leads to the energy splitting between them. This difference is demonstrated by the calculated spin densities for hyperfine-split bands, shown in Fig. 3(b).

Nuclear spin polarization can be understood using classical arguments. Consider the hydrogen atom H_2 rotating around an axis aligned with the S- H_1 bond. This rotation generates a magnetic field at the position of the H_1 nucleus on the rotational axis, polarizing its nuclear spin either parallel or antiparallel to the field direction, as illustrated in Fig. 4(a). The two hydrogen nuclei, one revolving on a larger orbit (H_2) and the other located on the rotational axis (H_1), are permutationally isolated. Hence, the spatial part of the total wave function is symmetric with respect to the exchange of the two hydrogen nuclei. To satisfy the Pauli exclusion principle, the antisymmetric character of the total wave function must reside in the spin component. As a result, the spin of the rotating

nucleus H_2 must be polarized in the opposite direction to that of the H_1 nucleus on the rotational axis.

As shown in Fig. 3(a), the hyperfine interaction repels (couples) states of the same parity, each of which has a degenerate state component of opposite parity. The coupling results in a hyperfine energy splitting that is slightly different for the positive-parity state pairs as compared to the negative-parity state pairs, effectively lifting the original degeneracy between opposite-parity states. For example, at $J = 50$, positive-parity B_2 symmetry cluster states of H_2S split by 3.613 MHz, while the negative-parity B_1 symmetry states split by 3.640 MHz. This 27 kHz difference causes two pairs of B_1 and B_2 cluster states, originally degenerate within 0.2 kHz, to shift apart by about 13.5 kHz. The same effect of hyperfine-induced lifting of parity degeneracy was observed in high-precision spectroscopic measurements of the ν_4 band of PH_3 [39] and the ν_3 band of SiH_4 [40] (for E-symmetry state pairs), as well as of the ν_3 band of SF_6 (for the A_{1g} - A_{1u} symmetry pairs) [38]. These molecules similarly exhibit rotational level clustering in the rotational bands probed in the experiments. The observed splittings between opposite-parity states ranged from 8 to 32 kHz, which is consistent with the present theoretical predictions for H_2S .

This effect can be understood using the picture of tunneling between different rotating enantiomers, induced by hyperfine interactions. From Eq. (2), it follows that the energy differences between opposite-parity hyperfine cluster states, e.g., $|1, B_2\rangle$ and $|1, B_1\rangle$, arise from nonzero coupling between L_1 and R_1 (or L_2 and R_2), or between L_1 and R_2 (and similarly L_2 and R_1). As noted earlier, the $L_1 \rightarrow R_2$ transition, which involves a rotation of approximately 90° around an axis perpendicular to the main rotational axis, is energetically more favorable than the $L_1 \rightarrow R_1$ transition. This motion effectively exchanges H_1 and H_2 combined with an inversion operation. Since the direction of rotation remains unchanged, the magnetic field induced at the nucleus located on the rotational axis remains the same, aligning the spin in the same direction. The spin of the rotating nucleus also remains oppositely aligned, as shown in Fig. 4(b). The H_1 and H_2 , however, alternate between being on the rotational axis and on an orbiting trajectory, which swaps their nuclear spin projections. Such transition can be facilitated by the spin-rotation coupling element, such as $\hat{J}_X \hat{J}_Y$. Here, the $\hat{J}_X$ operator flips the spins, while the $\hat{J}_Y$ alters the projection of the rotational angular momentum, resulting in an enhanced precession of the S- H bond about the rotational axis, which favors the $L_1 \rightarrow R_2$ transition.

Interestingly, if the Pauli exclusion principle were disregarded, the spin polarization of the proton on an orbiting trajectory would be zero, and the tunneling $L_1 \rightarrow R_2$ depicted in Fig. 4(b) would be forbidden. In this case, the degeneracy of opposite-parity states would not be lifted. This conclusion aligns with experimental observations of hyperfine-induced parity degeneracy lifting in SF_6 , PH_3 , and SiH_4 [39,40,57], where the authors emphasize that this phenomenon can be seen as a consequence of the Pauli exclusion principle forbidding two degenerate states differing only by parity.

In the absence of hyperfine interactions, the rotating enantiomers originating from rotations about the S- H_1 or S- H_2 bonds are indistinguishable. However, hyperfine interactions

introduce an additional chiral center—the nuclear spin, which, combined with rotational chirality, gives rise to two chiral diastereomers. Much like chemical diastereomers, these states have different energies and also opposite orientations of the nuclear spin projections onto the rotational axis. These diastereomers, however, cannot be assigned as rotating about a specific bond (i.e., L_1 or L_2); rather, they represent a coherent mixture of rotations about both S–H bonds. Further details and Stark-effect simulations for spin-induced diastereomers are provided in the Supplemental Material [45].

The demonstrated effect of spin symmetry breaking in rotational energy level clusters is not merely a result of near-degeneracy of cluster states; i.e., it does not occur in other similarly closely degenerate states with symmetry-allowed hyperfine interactions. Instead, it emerges from the unique rotational character of these states, isolating identical nuclei on different, nonoverlapping trajectories. Hyperfine interactions facilitate tunneling between rotating enantiomers, a phenomenon intrinsically tied to the Pauli exclusion principle. This mechanism accounts for previous spectroscopic observations of parity-degeneracy lifting in molecules exhibiting rotational clustering, which can serve as direct experimental evidence for the predicted effect. More broadly, this phenomenon is expected to be a general characteristic of hyperfine interactions in systems exhibiting molecular-

frame localization of rotational axis and rotational ergodicity breaking [37].

Although populating rotational cluster states in small molecules like H_2S requires tailored laser fields [21], larger molecules, such as fullerene C_{60} , can significantly populate states with rotational axis localization even at room temperature. We also predicted the existence of rotational cluster states at much lower angular momenta in vibrationally excited bending bands of H_2S . Specific rotating enantiomers can be selectively prepared by interacting the molecule with a chiral field, for example, an optical centrifuge combined with a static electric field aligned along the centrifuge's k vector [7,23]. Nuclear spin polarization can be indirectly measured using ion velocity-map imaging, as it is preserved in atomic fragments after photodissociation and influences both the electronic spin and fragmentation dynamics through hyperfine interactions [58–60].

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Data availability. The data that support the findings of this article are openly available [53], embargo periods may apply.

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