Hyperfine-Induced Lifting of Parity Degeneracy in Noninverting Molecules

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We report experimental evidence for the splitting of \(E\) levels in \(^{28}\text{SiF}_4\), which are degenerate in parity as far as the rovibrational Hamiltonian solely is concerned. The parity degeneracy of rovibrational levels is in fact lifted by hyperfine interactions, even though the associated total spin is \(I = 0\). We compare this situation with that in other molecules (SF\(_6\) and PH\(_3\)) for which similar effects have already been reported. We also predict the splitting of the \(P(7)\) \(E^0(\pm)\) line of \(^{13}\text{CH}_4\), a resonance used currently as a frequency standard, assumed up to now to be perfectly degenerate.

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Inversion of all space coordinates of every particle belonging to a given physical system is a relevant symmetry as long as weak interactions are not taken into account. Two stationary states completely identical, but for parity, in a semirigid (i.e., noninverting) molecule, should be perfectly degenerate. Such parity degenerate molecular states thus represent excellent candidates to detect a parity violating interaction, which should result in their splitting.

We have observed such a splitting of parity degenerate \(E\) states of the molecule \(^{28}\text{SiF}_4\). Although the total spin of the fluorines is zero, we show that hyperfine couplings with neighboring states are responsible for this splitting. A similar lifting of parity degeneracy has already been observed in the spectrum of SF\(_6\) [2,3,9,10] but different from the PH\(_3\) case for which an \(E\) splitting was observed for an isolated line [11]. To understand these differences, we analyze below the structure of the wave functions in these various cases.

A closer look at \(^{28}\text{SiF}_4\) \(E(\pm)\) wave functions.—The total molecular wave function may be qualitatively written, in the Born-Oppenheimer approximation, as a tensor product of electronic, vibrational, rotational, and nuclear spin terms, \(\Psi = \Psi_e \Psi_v \Psi_r \Psi_s\). The molecules that we consider here are always in a nondegenerate ground electronic state, and we will also be able to place ourselves in the ground vibrational state without any loss of generality. We thus forget here about the electronic and vibrational problems.

Since every member in the product has one definite parity, then so has \(\Psi\). The case of the rotational wave function stands apart, however, in the approximate case of

![Fig. 1. The \(R(34)\) \(F_{1(\pm)}^0 E^0 F_{1(\pm)}^0\) cluster. Theoretical spectra are displayed above experimental ones. \(F_{1(\pm)}^0\) levels are not parity doublets; \(F_{1(\pm)}^0\) in \(T_d \otimes C_i\) are, respectively, \(F_{1(\pm)}\) and \(F_{2(\pm)}\) in \(O \otimes C_i\). One should also recall here that Berger’s \(n\) label (here \(= 0\)) is labeling levels with respect to group \(O\).](image-url)
a rigid \(XY_4\) molecule, \(\Psi_r\) is the wave function of a rigid spherical top, 
\[
\Psi_{r \text{inv}}^{(J)}(\omega) = \sqrt{[J]!8\pi^2} \mathcal{D}_{MK}^{(J)w}(\omega)
\]
[using the formalism of irreducible tensors in \(L\text{SO}(3) \otimes M\text{SO}(3)\) [10,12,13], where \(\omega = (\alpha, \beta, \gamma)\) are the three Euler angles which bind the molecular and laboratory reference frames together. We now make our definition of inversion precise: \(I\) inverts simultaneously both the molecular and laboratory reference frames (exchanging right- and left-hand frames), leaving invariant the three Euler angles.

Thus, in order to describe completely the rotational wave function, one needs to add the label of the type of frame. One may formally define two sets of such wave functions [14]: one with respect to right-hand frames (\(\Psi_r^R\)), and one with respect to left-hand frames (\(\Psi_r^L\)), and finally build \(L\text{O}(3) \otimes M\text{O}(3)\) wave functions with defined parities,
\[
\Psi_{MK}^{(J)} = [\Psi_{rMK}^{R(J)}(\omega) \pm \Psi_{rMK}^{L(J)}(\omega)]/\sqrt{2}.
\]
(The only wave functions to be considered have the same parity in both groups.) If we neglect the inversion of the molecule, both sets have exactly the same energy: descriptions in right- and left-hand frames are equivalent.

Now let us consider the case of a semirigid \(XY_4\) molecule, where the symmetry is no more spherical but tetrahedral [\(T_d \subset M\text{O}(3)\)]. One may first use the group chain \(O \subset M\text{SO}(3) \subset M\text{O}(3)\), where \(O\) is the cube rotation group (isomorphic to \(T_d\)). Thus, the rotational wave functions \(\hat{\Psi}_r\), symmetry adapted in \(O\), are parity-independent linear combinations of the rigid wave functions [15],
\[
\hat{\Psi}_{rMK\sigma}^{(J,J,nC)} = \sum_{K=-J}^{J} G_{nC\sigma}^{K} \Psi_{MK}^{(J,J,nC)}.
\]
\(C_r\) stands for \(O\)'s irreducible representations (ir), \(\sigma_r\) for \(C_r\)'s components, and \(n\) is numbering identical \(C_r\). Again, the \((\pm)\) rotational wave functions in (2) are truly parity degenerate. These wave functions also form ir of \(T_d\), but the correct labeling adapted to the \(T_d\) point group will require one to be more precise about the isomorphism between \(O\) and \(T_d\).

But before, we have to introduce the spin symmetries \(C_s\) which are easily found, given that \(^{28}\text{Si}\) has no spin, and that \(F\) nuclei have a spin \(1/2\) [7]: This gives \(C_s = A_1, F_2, \text{ or } E\), which correspond, respectively, to values \(I = 2, 1\), and \(0\) for the total nuclear spin.

One finally has to couple \(\hat{\Psi}_r\) with the nuclear spin wave function \(\Psi_s\) in order to obtain the total molecular states \(\Psi\). Then, the Fermi-Dirac statistics constrains the overall symmetry of the existing states \(\langle \Psi \rangle\) to be \(A_2\) in \(T_d\). All this is summarized below:

<table>
<thead>
<tr>
<th>(C_r), (\tau) in (O \otimes C_t)</th>
<th>(C_r), (\tau) in (T_d \otimes C_t)</th>
<th>(C_s) in (T_d)</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1(\pm))</td>
<td>(A_1(\pm))</td>
<td>(A_1)</td>
<td>(A_1)</td>
</tr>
<tr>
<td>(A_2(\pm))</td>
<td>(A_2(\pm))</td>
<td>(A_2)</td>
<td>(A_2)</td>
</tr>
<tr>
<td>(E(\pm))</td>
<td>(E(\pm))</td>
<td>(E)</td>
<td>(E_2), (A_1), (F_2)</td>
</tr>
<tr>
<td>(F_1(\pm))</td>
<td>(F_1(\pm))</td>
<td>(F_2)</td>
<td>(A_2), (E_2), (F_2)</td>
</tr>
<tr>
<td>(F_2(\pm))</td>
<td>(F_2(\pm))</td>
<td>(A_1), (E_2), (F_2)</td>
<td></td>
</tr>
</tbody>
</table>

This table shows, for example, the correspondences \(A_1(+) \leftrightarrow A_1(+), \quad A_2(-) \leftrightarrow A_2(-), \quad E(+) \leftrightarrow E(+), \quad E(-) \leftrightarrow E(-)\) between \(O\) and \(T_d\) representations. More precisely, a consistent orientation of the \(E\) representations in the \(T_d\) point group requires the following definitions [15]:

\[
\Psi_{rMK\sigma}^{(J,J,nE)} = \hat{\Psi}_{rMK\sigma}^{(J,J,nE)}(3a),
\]
\[
\Psi_{rMK\sigma}^{(J,J,nE)} = (-1)^{\sigma} \hat{\Psi}_{rMK\sigma}^{(J,J,nE)}(3b).
\]
Hyperfine Hamiltonian. We have shown that tensor terms give rise to different hyperfine energies for the hyperfine components of opposite parity, a difference which can only be explained by the different structure of the rovibrational part between the two states similar to the case of SiF$_6$ [cf. Eqs. (3a) and (3b)], but in SiF$_4$ these diagonal terms are 0 because $I = 0$. Otherwise, we would have both origins for the splitting. This would be the case in CD$_4$, for example.

In conclusion, we have observed for the first time a hyperfine splitting of $E_{(+)}(I = 0)$ states in $^{28}$SiF$_4$. Such a lifting of parity degeneracy was previously observed in SF$_6$ and PH$_3$. The comparative analysis of the hyperfine mechanisms revealed that the common and key feature of these situations is that it is not possible to build two total wave functions which satisfy the Pauli principle and differ only by parity: a difference in the structure of the rotational wave functions for the $E$ states (SiF$_4$, PH$_3$), different nuclear spin wave functions for the $A_{1g}$-$A_{1u}$ states (SF$_6$).

Thus, the hyperfine tensor interactions can lift the parity degeneracy if the total spin is nonzero because of diagonal terms (case of PH$_3$) or, if $I = 0$ (case of $E$ states in $^{28}$SiF$_4$ and $A_{1g}$-$A_{1u}$ states in SF$_6$), because of couplings with neighbors of different rovibrational symmetry or for both reasons (case of $F_{1g}$-$F_{1u}$ states in SF$_6$).

This result has important metrological consequences for $^{12}$CH$_4$, which is a molecule similar to $^{28}$SiF$_4$. In the $P(7)A_{2g}^{0(+)2}F_{1(-)}$ superfine cluster of methane, the $E$ line is far from its neighbors (3 GHz from $F_{1(-)}$, 9 GHz from $A_{2g}^{0(+)2}$), nevertheless, we have calculated that hyperfine couplings should induce a 20 Hz splitting as in $P(22)A_{2g}^{0(+)2}F_{1(-)}E$ of $^{28}$SiF$_4$ (Fig. 2). This very small splitting between the two $E$ states of opposite parity.
is comparable to the highest resolution of the latest measurements of the $P(7) F_{1}^{(-)}$ line at 3.39 $\mu$m [19]. The slightly different intensity of the two components induces an asymmetry of the unresolved doublet which depends on the experimental conditions. Thus, this effect could be responsible for a systematic shift of the measured frequency of such a line, which has never been considered in the past.