Hyperfine-Induced Lifting of Parity Degeneracy in Noninverting Molecules

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We report experimental evidence for the splitting of E levels in $^{28}\mathrm{SiF}_4$, 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 $^{12}\mathrm{CH}_4$, a resonance used currently as a frequency standard, assumed up to now to be perfectly degenerate. [S0031-9007(96)00392-4]

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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 $^{28}\mathrm{SiF}_4$. 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 and PH_3. We analyze in detail the different mechanisms involved. We point out that, in all cases, the Pauli principle forbids the existence of identical states but for parity in such molecules, and, thus, any degeneracy may be removed by mechanisms different from inversion and weak interactions.

Extensive saturation spectra of the ν_3 vibration-rotation band of $^{28}\mathrm{SiF}_4$ have been recorded in our laboratory with our ultrahigh resolution saturation spectrometer [1–5]. The current linewidth for these spectra was 1.5 kHz. We have used various isotopic species of CO_2 and a microwave electrooptic modulation technique [5] in order to increase the spectral coverage. In previous studies of SiF_4 [6], the hyperfine structure of the lines could not be resolved. Figures 1 and 2 display, respectively, the hyperfine structures of the $R(34)F^0_{1(-)}E^0F^0_{1(+)}$ and $P(22)A^1_{2(+)}F^5_{1(-)}E^3$ superfine clusters.

It is well known that the Pauli principle limits drastically the number of existing states: The F_1 and A_2 rovibrational states are associated with total nuclear spins I respectively equal to 1 and 2 and give rise to partly resolved triplets and quintuplets in these spectra; moreover, only one of the two parity states is allowed. On the other hand, E states are associated with $I = 0$ and may have both parities [7,8]. The observed splitting of the E lines correspond necessarily to the two parity labels. As we shall see, this degeneracy removal is related to the neighbor hyperfine states (with a symmetric neighborhood for Fig. 1 and an asymmetric one for Fig. 2). For isolated E lines no such splitting is observed, e.g., $R(17)E^0$. This is comparable to what was observed for the u-g splittings in 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 $^{28}\mathrm{SiF}_4$ $E_{(\pm)}$ *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 Ψ. The case of the rotational wave function stands apart, however, in the approximate case of

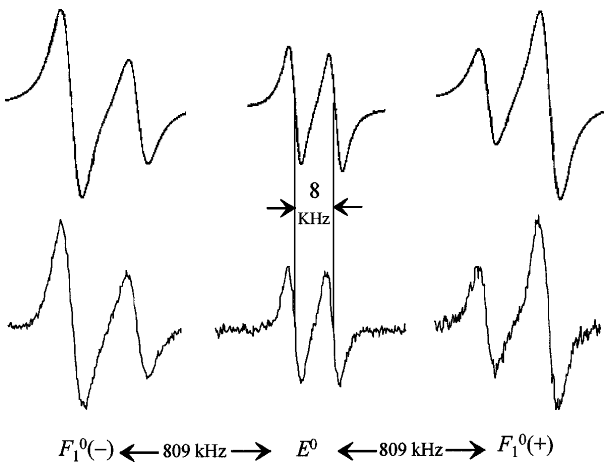

FIG. 1. The $R(34)\,F^0_{1(-)}E^0F^0_{1(+)}$ cluster. Theoretical spectra are displayed above experimental ones. $F^0_{1(\pm)}$ levels are not parity doublets: $F_{1(\pm)}$ in $\mathrm{T}_d \otimes C_i$ are, respectively, $F_{1(+)}$ and $F_{2(-)}$ in $\mathrm{O} \otimes C_i$. One should also recall here that Berger's n label (here = 0) is labeling levels with respect to group O.

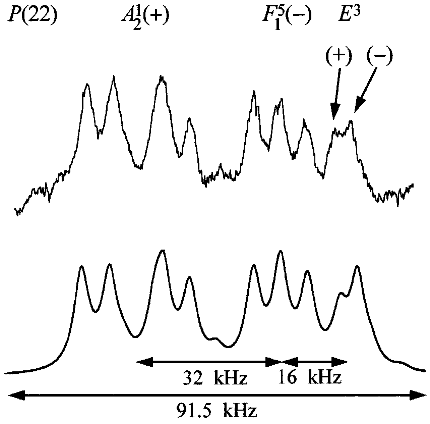

FIG. 2. The $P(22)\,A^1_{2(+)}F^5_{1(-)}E^3$ cluster. Top, experimental saturation spectrum. Bottom, theoretical calculation.

a *rigid* XY_4 molecule, Ψ_r is the wave function of a rigid spherical top,

$$\Psi^{(J,J)}_{r_{MK}}(\omega) = \sqrt{[J]/8\pi^2}\,\mathcal{D}^{(J)*}_{MK}(\omega)$$

[using the formalism of irreducible tensors in ${}^L\mathrm{SO}(3) \otimes {}^M\mathrm{SO}(3)$ [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 (Ψ^R_r), and one with respect to left-hand frames (Ψ^L_r), and finally build ${}^L\mathrm{O}(3) \otimes {}^M\mathrm{O}(3)$ wave functions with defined parities,

$$\Psi^{(J_\pm,J_\pm)}_{rM\,K} = [\Psi^{R(J,J)}_{r\,M\,K}(\omega) \pm \Psi^{L(J,J)}_{rM\,K}(\omega)]/\sqrt{2}\,. \qquad (1)$$

(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 [$\mathrm{T}_d \subset {}^M\mathrm{O}(3)$]. One may first use the group chain $\mathrm{O} \subset {}^M\mathrm{SO}(3) \subset {}^M\mathrm{O}(3)$, 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],

$$\hat{\Psi}^{(J_\pm,J_\pm nC_r)}_{rM\sigma_r} = \sum_{K=-J}^{J} {}^{(J)}G^K_{nC_r\sigma_r}\,\Psi^{(J_\pm,J_\pm)}_{rMK}\,. \qquad (2)$$

C_r stands for O's irreducible representations (ir), σ_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 ${}^{28}\mathrm{Si}$ has no spin, and that F nuclei have a spin 1/2 [7]: This gives $C_s = A_1$, F_2, or E, which correspond, respectively, to values $I = 2$, 1, and 0 for the total nuclear spin.

One finally has to couple Ψ_r with the nuclear spin wave function Ψ_s in order to obtain the total molecular states Ψ. Then, the Fermi-Dirac statistics constrains the *overall* symmetry of the existing states (Ψ) to be A_2 in T_d. All this is summarized below:

C_r, τ in $\mathrm{O} \otimes C_i$	C_r, τ in $\mathrm{T}_d \otimes C_i$	C_s in T_d	Overall
A_1 $(\pm)$	$\cancel{A}_1(+)$	A_1	$\cancel{A}_1$
	$A_2(-)$	A_1	A_2
A_2 $(\pm)$	$A_2(+)$	A_1	A_2
	$\cancel{A}_1(-)$	A_1	$\cancel{A}_1$
E $(\pm)$	$E(+)$	E	A_2, $\cancel{A}_1$, $\cancel{E}$
	$E(-)$	E	A_2, $\cancel{A}_1$, $\cancel{E}$
F_1 $(\pm)$	$F_1(+)$	F_2	A_2, $\cancel{E}$, $\cancel{F}_2$
	$\cancel{F}_2(-)$	F_2	$\cancel{A}_1$, $\cancel{E}$, $\cancel{F}_1$
F_2 $(\pm)$	$\cancel{F}_2(+)$	F_2	$\cancel{A}_1$, $\cancel{E}$, $\cancel{F}_1$
	$F_1(-)$	F_2	A_2, $\cancel{E}$, $\cancel{F}_2$

This table shows, for example, the correspondences $A_{1(+)} \longleftrightarrow A_{1(+)}$, $A_{1(-)} \longleftrightarrow A_{2(-)}$, $E_{(+)} \longleftrightarrow E_{(+)}$, $E_{(-)} \longleftrightarrow E_{(-)}$ 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]:

$$\Psi^{(J_+,J_+nE)}_{rM\sigma} = \hat{\Psi}^{(J_+,J_+nE)}_{r_{M\sigma}}, \qquad (3a)$$

$$\Psi^{(J_-,J_-nE)}_{rM\sigma} = (-1)^\sigma\,\hat{\Psi}^{(J_-,J_-nE)}_{rM3-\sigma}\,. \qquad (3b)$$

σ holds for 1 or 2, the components of the E representation. Ψ_r and $\hat{\Psi}_r$ refer, respectively, to T_d and O. The table shows also that only the T_d symmetries A_2, E, F_1 of the rovibrational states are allowed, and among these only the E states will yield a parity degeneracy. With these $E_{(\pm)}$ representations, we can build two total wave functions of symmetry A_2 [$F(= J$, here) being the total angular momentum, and J the total orbital angular momentum]

$$\Psi^{(F_\pm,nA_2)} = \Psi^{(J_\pm,J_\pm nE)}_{r1}\Psi^{(0,E)}_{s2} - \Psi^{(J_\pm,J_\pm nE)}_{r2}\Psi^{(0,E)}_{s1}\,.$$

The key point for the discussion below is to note that these two wave functions differ by more than parity, as is clear from Eqs. (3a) and (3b). This is because the G coefficients [cf. Eq. (2)] involved in the expression of the $(+)$ and $(-)$ wave functions are now different in the T_d point group.

This situation is actually the same as in the case of the E states of PH_3, for which we have also shown that the entanglement of the rovibrational and the nuclear spin wave functions differs from the $E(+)$ and $E(-)$

states [11]. This is true for each hyperfine component, the total spin of hydrogen being $I_H = \frac{1}{2}$. For SF_6, for which the point group is $O_h = O \otimes C_i$, the rotational wave functions are simply given by Eq. (2) where $C_r(+)$ $[C_r(-)]$ representations are now called C_{rg} $[C_{ru}]$. For example, let us consider A_{1g} and A_{1u} rotational states. The Pauli principle imposes the A_{2u} symmetry for the total wave functions,

$$\Psi^{(F_+,A_{2u})} = \Psi_r^{(J_+,J_+nA_{1g})}\Psi_s^{(0,A_{2u})},$$
$$\Psi^{(F_-,A_{2u})} = \Psi_r^{(J_-,J_-nA_{1u})}\Psi_s^{(0,A_{2g})}.$$

The rotational wave functions differ only by parity. However, this is not the case for the total wave functions, since the spin wave functions are different, although the total spin of the fluorine nuclei is 0 in both cases. (The parity of the spin wave functions, which is governed by the intrinsic parity of the S nucleus, is constant and does not play any role here.) Now, the E parity degeneracy in SiF_4 and PH_3 and the A_{1g}-A_{1u} parity degeneracy in SF_6 will be lifted if hyperfine interactions can discriminate between the total wave functions, as we see now.

Hyperfine couplings.—For the three molecules considered, we call G the corresponding point group. The hyperfine Hamiltonian is dipolar magnetic: $H_{\mathrm{HF}} = -\boldsymbol{\mu} \cdot \mathbf{B}$. It subdivides into spin-orbit (spin-rotation and spin-vibration) and spin-spin terms, which can be written, in the group chain ${}^{L}O(3) \otimes [{}^{M}O(3) \supset G]$ [10,13], as couplings of rovibrational and nuclear spin operators of the form

$$H_{\mathrm{HF}}^{(0_+,A_1)} = [H_{RV}^{(k_+,k'_+C)}H_{NS}^{(k_+,C)}]^{(0_+,A_1)}.$$

A_1 stands for the totally symmetric representation of the group G. H_{HF} subdivides then in *scalar* and *tensor* terms, depending on whether $C = A_1$ or not. In the case of SiF_4 and SF_6, the total spin is 0 and the states have no hyperfine energy. However, the structure of the tensor terms indicates that they can couple states of different C_r and C_s and different values of I (but the same F and same parity) [1,9]. The different couplings are illustrated in Fig. 3 in the case of SiF_4. When rovibrational levels are clustered, the effect of these couplings becomes important and lifts the parity degeneracy of A_{1g}-A_{1u} [2,3], F_{1g}-F_{1u} [9,10], or E doublets which are, actually, contaminated by neighboring rovibrational states of other symmetries. [In the case of F_{1g}-F_{1u} of SF_6, besides this effect of nearby F_{2g} levels, there is already a difference in diagonal terms of the hyperfine Hamiltonian due to the difference in spin wave functions (cf. Fig. 2 of [10]).] This is well described by T_d or O_h symmetry breaking induced by rovibrational effects, such as the centrifugal distortion, which are effectively responsible for this clustering of rovibrational levels [16–18]. Figures 1 and 2 show two clusters of SiF_4 in which the E doublet is resolved.

In PH_3 [11], for which the $E_{(\pm)}$ rovibrational doublet is well isolated, the previous explanation is not relevant. One must consider only the diagonal terms of the 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_4 [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.

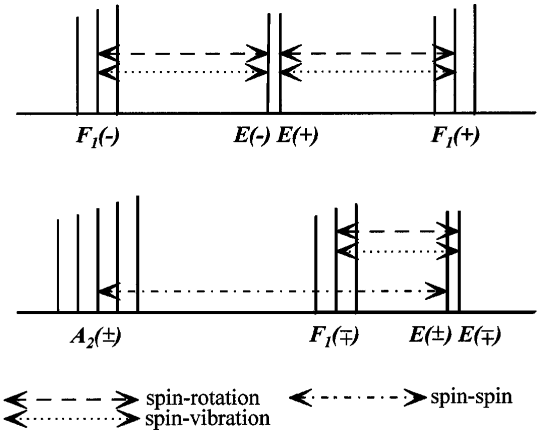

FIG. 3. "Isolated" hyperfine structures and hyperfine couplings allowed inside the superfine clusters containing E levels. (The $E_{(+)}$ and $E_{(-)}$ levels have been artificially split here for more clearness.) The hyperfine levels of a superfine level are labeled by parity and by the total angular momentum F ($\mathbf{F} = \mathbf{J} + \mathbf{I}$). Two states differing by at least one of these two labels cannot be coupled.

In conclusion, we have observed for the first time a hyperfine splitting of $E_{(\pm)}$ ($I = 0$) 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 $P(7)\,A^0_{2(+)}F^1_{1(-)}E^0$ superfine cluster of methane, the E^0 line is far from its neighbors (3 GHz from $F^1_{1(-)}$, 9 GHz from $A^0_{2(+)}$), nevertheless, we have calculated that hyperfine couplings should induce a 20 Hz splitting as in $P(22)\,A^1_{2(+)}F^5_{1(-)}E^3$ 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 $P(7)\,F^1_{1(-)}$ line at 3.39 μm [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.

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