

Hyperfine Lifting of Parity Degeneracy and the Question of Inversion in a Rigid Molecule

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This Letter demonstrates that the parity degeneracy of isolated vibration-rotation states of a rigid molecule can be removed by hyperfine interactions. Hyperfine structures of infrared transitions in PH_3 are obtained by saturation spectroscopy around $10\ \mu\text{m}$. One of these is used to demonstrate unequivocally that degenerate states of opposite parity are separated by the proton hyperfine interactions. We show that alternative explanations involving the physical inversion of the molecule are completely inconsistent with the details of the spectra obtained. In addition to the splitting conclusion, which has very wide generality, new confidence limits are placed on the possible inversion splitting.

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The degrees of freedom of most molecules in their ground electronic levels can be divided among translations, vibrations, rotations, large amplitude motions, and nuclear spin. Among large amplitude motions inversion plays a peculiar role since parity, the associated quantum number, is always good because of the invariance property of space under inversion in the absence of weak interactions. When a molecule inverts freely it is not surprising to find that the degeneracy of levels of opposite parity is lifted. The first important result of this paper is to show experimentally, via the example of phosphine, that the degeneracy will be lifted even for a rigid molecule in which there is no inversion. We show, further, that this result is intimately connected to the Pauli principle and that there can be no essential degeneracy with parity.

Following earlier work on hyperfine effects in ammonia, we will classify the vibration-rotation and hyperfine states of a rigid molecule such as phosphine (PH_3) under the geometrical point group C_{3v} [1,2] and use the Landau [3] and Berger [4] notations. The rovibrational states are characterized by quantum numbers J and k for total orbital angular momentum and its component along the symmetry axis, respectively, while $K=|k|$. v is the quantum number for vibrational excitation, and l is the quantum number for the corresponding component of angular momentum along the symmetry axis. Thus, for example, the degenerate v_4 state excited to the level $v_4=1$ has $l=\pm 1$. Finally, the parity, $\tau=(\pm)$, completes the description of the rovibrational states. For symmetric top molecules, it is convenient to introduce the symmetric (s) and antisymmetric (a) character of a state upon reflection in a plane perpendicular to the symmetry axis. The correspondence between τ and v is $\tau=(+)$ if $v=(s)$ and K even or if $v=(a)$ and K odd; otherwise, $\tau=(-)$. States having $k-l=\pm 3n$ form a representation A_1+A_2 except when $k-l=0$, the states then being either A_1 or A_2 depending upon J and τ . States having $k-l=\pm(3n+1)$ or $\pm(3n+2)$ are of symmetry E . I_P , the

nuclear spin of ^{31}P , is $\frac{1}{2}$ and the corresponding symmetry must necessarily be A_1 as the atom is certainly on the symmetry axis. Then, the total proton spin, I_H , must be included. Proton spin states with $I_H=\frac{1}{2}$ and $I_H=\frac{3}{2}$ form E and A_1 representations, respectively. We bear in mind that the final wave function must be antisymmetric with respect to exchange of any pair of protons; i.e., it must be of symmetry A_2 .

Consider first the states such that k is a multiple of 3 (we ignore the vibrational degrees of freedom and the Zeeman degeneracy which do not matter here). We can build the following states:

$$(1/\sqrt{2})(|J, K, v\rangle \pm (-1)^{J+v}|J, -K, v\rangle),$$

which is of symmetry A_1 or A_2 according to whether the $+$ or $-$ sign is taken [by convention, $(-1)^{(s)}=+1$ and $(-1)^{(a)}=-1$]. In this case, the Pauli principle imposes that the nuclear spin wave function should be A_1 ($I_H=\frac{3}{2}$) and only the A_2 coordinate states are allowed. The above expressions show that the $A_2(+)$ and $A_2(-)$ states differ not only by the parity but also by their rotational structure. We can check that, for $K=0$, only one state exists which is $A_2(+)$ for odd J and $A_2(-)$ for even J . Various terms, for example, centrifugal distortion, Coriolis, and l -doubling terms in some vibrationally excited states, couple states with $\Delta k \neq 0$. Thus, only one subset of given parity will be perturbed by the $K=0$ state, and hence $A_2(+)$ and $A_2(-)$ states are split for $K \neq 0$. This $A_2(-)$ - $A_2(+)$ splitting (A_1 - A_2 splitting in the permutation-inversion group notation [5]) has been observed in PH_3 [6] but certainly does not imply any molecular inversion.

The case of states such that $k-l$ is not a multiple of 3 is more subtle. An E rovibrational level can be combined only with an E nuclear level (which implies $I_H=\frac{1}{2}$), which results in only *one allowed* hyperfine state as the decomposition of $E \times E$ gives A_1+A_2+E . Since $I_H=I_P=\frac{1}{2}$, four hyperfine states are predicted in total and any corresponding spectrum will have four main lines. Now

there are two E rovibrational levels differing only by parity and this doubles the number of states. However, inversion cannot play any role for a rigid molecule and thus, at first sight, we anticipate just four states, each one being twofold degenerate because of parity.

Figure 1 shows the ${}^R P_2(10)$ transition of the ν_4 band of PH_3 obtained by saturation spectroscopy using CO_2 lasers. The residual linewidth is about 3 kHz (HWHM) and reproducibility of splittings is better than 200 Hz [7,8]. The vibration-rotation symmetry is certainly E but the transition displays *eight* components, twice the number anticipated. This spectrum shows the first example of the breaking of parity degeneracy of E states induced by hyperfine interactions in a rigid molecule and not by inversion as we now demonstrate.

In order to illustrate the role of the Pauli principle, we will express the expanded forms of the A_1 and A_2 total wave functions which will reveal clearly the origin of their differences. We consider a rotational level with a well defined value of K , omitting the phosphorus spin ket and the quantum number of the projection of J on a fixed axis as these do not affect the argument. A typical wave function can be written as

$$\frac{1}{\sqrt{6}} [(|K, v\rangle \pm (-1)^{J+v} | -K, v\rangle) | - + +\rangle + \varepsilon (|K, v\rangle \pm (-1)^{J+v} \varepsilon | -K, v\rangle) | + - +\rangle + \varepsilon^2 (|K, v\rangle \pm (-1)^{J+v} \varepsilon^2 | -K, v\rangle) | + + -\rangle]$$

if $K \equiv 1$ [3], and

$$\frac{1}{\sqrt{6}} [(| -K, v\rangle \pm (1)^{J+v} |K, v\rangle) | - + +\rangle + \varepsilon (| -K, v\rangle \pm (-1)^{J+v} \varepsilon |K, v\rangle) | + - +\rangle + \varepsilon^2 (| -K, v\rangle \pm (-1)^{J+v} \varepsilon^2 |K, v\rangle) | + + -\rangle]$$

if $K \equiv 2$ [3], where $+$ corresponds to an A_1 state and $-$ to an A_2 state; $\varepsilon = e^{2i\pi/3}$ and $| - + +\rangle$ is the ket representing projections $-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ of the three protons onto a fixed axis. This form of the wave function shows explicitly that $A_1(+)$ and $A_2(-)$ states differ only by the total parity and, thus, have the same hyperfine energy. By contrast, $A_2(+)$ and $A_2(-)$ states have different rotational structures as well as different parities. Similar reasoning can be used for the $A_1(-)$ and $A_2(+)$ states.

Figure 2 displays the level structure for a particular value of F_1 and F for an E vibration-rotation state where F_1 and F correspond to the most convenient coupling scheme: $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_p, \mathbf{F} = \mathbf{F}_1 + \mathbf{I}_H$. As noted before, we start with eight states, derived from factors of 2 for E vibration-rotation level, E spin wave functions, and parity (\pm). One obvious route by which the parity degeneracy might be lifted is tunneling [Fig. 2(a)], by direct analogy with the well-known case of ammonia [1,9], and there have been numerous attempts to observe this possibility [10,11]. The degeneracy can be further lifted through the hyperfine interactions [Fig. 2(b)]: Tensorial hyperfine terms in the Hamiltonian couple kets $|k, v\rangle$ such that $\Delta k = \pm 2$ and we can see from the above wave functions that, if $K=1$, these give diagonal matrix elements of opposite sign for $A_2(+)$ - $A_1(-)$ and $A_2(-)$ - $A_1(+)$ states, hence the splitting. By contrast with the case of K a mul-

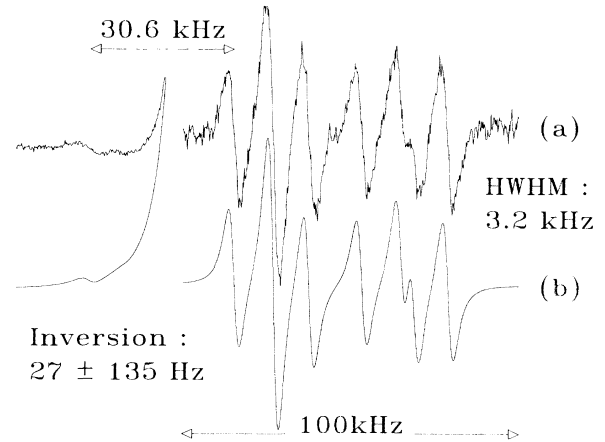


FIG. 1. (a) Saturation spectrum of $\nu_4 {}^R P_2(10)$ obtained with a CO_2 laser operating on $9P(18)$. Typical gas pressures and laser powers are 5×10^{-5} Torr and $5 \mu\text{W}$ for the main lines, 2×10^{-4} Torr and $500 \mu\text{W}$ for the crossovers. (b) Corresponding calculated spectrum. The differential saturation between the main lines and the crossovers is not taken into account.

multiple of 3, no coupling with other rovibrational states is required. Detailed study of the rotational structure of the split states reveals that, for the two situations, the molecular axis acquires essentially two orthogonal directions well defined relative to the fixed frame. Thus, the phosphorus spin and the molecular rotation induce magnetic fields which will be different at the proton locations. The Pauli principle requires that only the two A_2 states survive [full lines in Fig. 2(b)]. Inversion splitting and hyperfine doubling might both be present; this is the case of the $K=1$ states of ammonia. For a rigid molecule, only hyperfine doubling can be present [Fig. 2(c)]. This corresponds to our situation, for which the $E(+)$ and $E(-)$ rovibrational levels reveal two different hyperfine structures, and thus eight lines are observed. The situation exposed here about the structure and the symmetry of the total wave functions has some common features with that for rovibrational wave functions with K a multiple of 3. In both cases, the Pauli principle forbids the coexistence of two states which differ only by parity. If we consider an allowed wave function (symmetry A_2) with a defined orbital parity τ , then change of this parity alone leaves the behavior under rotations preserved. By contrast, the behavior under improper operations of the point group (like a planar reflection of C_{3v} which ex-

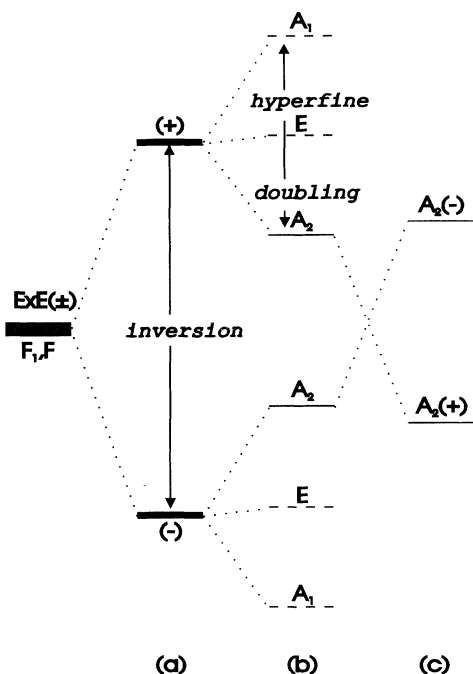


FIG. 2. Rovibrational states of symmetry E and parity $(+)$ or $(-)$ for given F_1 and F . Such a level is 8 times degenerate: symmetry E of the rovibrational state, symmetry E of the nuclear state, and total parity (\pm) . (a) The inversion can split states of opposite parity. (b) Each sublevel (\pm) presents the same hyperfine structure. A_1, E, A_2 are the symmetries of the total wave functions in the C_{3v} group. Dashed lines correspond to forbidden states. (c) For a rigid molecule like phosphine, only the second effect exists and the allowed $A_2(+)$ and $A_2(-)$ states thus reveal a hyperfine doubling.

changes two H's and is geometrically the product of inversion by a rotation) does change, and the wave function becomes A_1 , which is forbidden. The generality of this property should be emphasized; a similar reasoning can be applied for molecules with bosonic particles (like ND_3) for which the allowed wave functions are A_1 . The property continues to hold if, at least, one improper operation of the geometrical point group corresponds to the exchange of identical nuclei, which is the case for a very large class of molecules.

The hyperfine Hamiltonian requires several parameters: R, S for the ^{31}P and ^1H spin-rotation interactions, T for the ^{31}P - ^1H spin-spin interaction, and U for the interaction between the ^1H spins [12,13]. Each of these is multiplied by a function of quantum numbers as determined by standard techniques of double Racah algebra [2,14]. In the case of hyperfine doubling, two sets of constants S_+, T_+ and S_-, T_- have to be introduced for the $E(+), E(-)$ levels, respectively.

The lower vibrational level of the $^R P_2(10)$ transition can be considered as a pure state; i.e., only rotational states $k = \pm 2$ are involved: No hyperfine doubling is ex-

pected. Now the upper vibrational level, $v_4=1$, is strongly mixed with the nearby $v_2=1$ by a Coriolis coupling in which the main term preserves $k-l$ [15]. Neglecting some smaller contributions, the normalized rovibrational wave function is

$$\begin{aligned} & -0.844|v_4=1, J=9, K=3, (+I)\rangle \\ & -0.433|v_4=1, J=9, K=1, (-I)\rangle, \\ & +0.271|v_2=1, J=9, K=2, (I=0)\rangle \\ & -0.138|v_4=1, J=9, K=2, (+I)\rangle + \dots \end{aligned}$$

States with $K=1$ participate in the wave function and are responsible for the observed hyperfine doubling. This example shows that hyperfine doubling is much more general than might be anticipated from the unique case of $K=1$ states of ammonia. It is not a trivial task to work out the relevant Hamiltonian in detail as some account should be taken of the direct vibration-spin coupling because of the vibrational angular momentum. However, as for spherical tops [16], effective spin-rotation constants in the upper level can describe the observed structure of a given rovibrational line. The match between observed and calculated spectra in Fig. 1 will be seen to be exact in every detail, including weak crossover resonances and all intensities [17]. The fit is well conditioned, and converges strongly even if all parameters are originally set to zero. Derived ground-state parameters (with standard errors) are $R_0=114.76(5)$, $S_0=-8.01(6)$, and $T_0=-0.882$ kHz, and are consistent with those from a molecular beam study [18] and with separate fits of various $10 \mu\text{m}$ spectra that we have obtained [19]. Averaged values in the upper state are $R_1=R_0+7.888(13)$, $S_1=S_0+0.305(19)$, and $T_1=T_0+0.189$, with differences $S_{1+}-S_{1-}=-2.718(32)$, $T_{1+}-T_{1-}=6.9(6)$ kHz. T_0 and T_1 are calculated from molecular geometry. An additional fit gives $R_{1+}-R_{1-}=2 \pm 29$ Hz, which represents a stringent test on the model as the anticipated value is zero. Further, no significant change of S_0 and T_0 for lower states of even and odd parity can improve the fit.

There might still be some lurking suggestion that tunneling is responsible for the spectrum observed, particularly since it will be enhanced in the v_2 state for which the normal mode is an umbrella motion [20]. We can dispel this notion, however, by two different considerations.

First, we have included the inversion possibility separately in our fit and discover a residual splitting of 27 ± 135 Hz in the upper state, while the ground-state value must be even smaller [10].

Second, we give in Fig. 3 a spectrum of the v_2 transition $^2 Q_{12}(14)$ for which $A_2(+)-A_2(-)$ splitting is negligible [15]. However, it should certainly be susceptible to splitting via tunneling. Eight hyperfine components are now anticipated ($I_{\text{H}}=\frac{3}{2}$) although splittings in upper and lower states must be very similar as $\Delta J=\Delta K=0$.

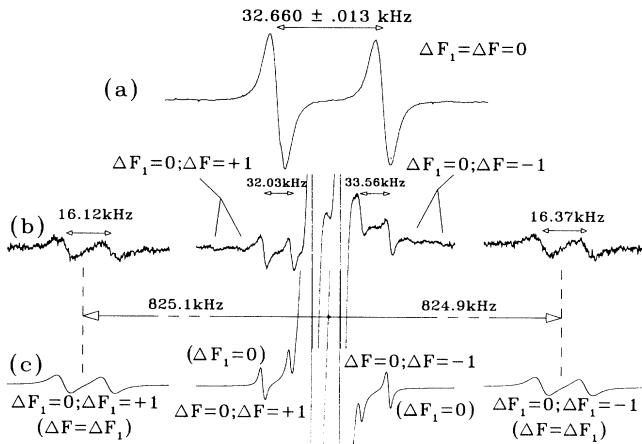


FIG. 3. (a) Weak-field saturation spectrum of $v_2 Q_{12}(14)$ obtained with a CO₂ laser operating on 10R(34). (b) Overview of the spectrum for strong laser field (1 mW) shows several sets of crossovers which have splittings equal to or half the main splitting. (c) The intensities of the theoretical spectrum match those of the crossovers. Note that the even weaker lines $\Delta F = \Delta F_1 = \pm 1$, visible on the experimental spectrum, do not show up on the theoretical one. For weak fields, the intensity ratio among main lines, crossovers, and these weak lines is typically $1000:1:10^{-3}$.

Thus, the strong transitions are interpreted as two groups having $\Delta F = \Delta F_1 = 0$ and a given value of F_1 , each comprising four proton components, separated by 32.66 kHz because of the change of the ^{31}P spin-rotation constant. This leads to a natural interpretation of the weak crossover resonances. The first sets appearing symmetrically in the wings of the strong lines reproduce the main structure and are obtained by combining two types of transitions $\Delta F = \Delta F_1 = 0$ and $\Delta F = \pm 1$, $\Delta F_1 = 0$. The second one implies a change in the proton spin orientation, and six crossovers overlap to form each observed line. Around ± 825 kHz from the main structure, two other sets of crossovers appear. They correspond to transitions $\Delta F = \Delta F_1 = 0$, $\Delta F = \Delta F_1 = \pm 1$ where a change in the phosphorus spin orientation is induced in the second case, and four crossovers overlap to form each line. The most crucial factor is that measured splittings within each crossover pair are 16.37(9) kHz and 16.12(13) kHz, so that the ratio to the main splitting (32.66 kHz) closely approximates 1:2, which is not consistent with any inversion in the upper state. The two main lines cannot be the inversion doublet, while the upper limit of inversion in the $v_2 = 1$ level is given by the linewidth which fits the $Q_{12}(14)$ spectrum.

This Letter provides the first, and unequivocal, observation of hyperfine splitting of levels of a rigid molecule which must be exactly degenerate under vibration-rotation symmetry. Earlier observation of $A_{1u}-A_{1g}$ splitting for the SF₆ molecule [21] and, more recently, $E(+)-E(-)$ splittings for a T_d molecule [22] both result from hyperfine mixing of nearby states, and hence involve rovi-

brational levels which are not isolated. Here, by contrast, the $E(+)$ and $E(-)$ states are isolated as the rovibrational parts of the total wave functions do not depend upon the strength of hyperfine interactions. We emphasize that the lack of parity degeneracy can be seen as a consequence of the Pauli principle which forbids one of a pair of states differing only in parity, a statement which is true for a wide variety of molecules. Two allowed molecular states which necessarily differ by more than parity will always be split if there is any term in the Hamiltonian which could reveal these differences, such as centrifugal distortion or tensorial hyperfine terms.

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