

Anomalous Spin-Rotation Coupling in the $X^2\Sigma^+$ State of YbF

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We have measured the spin-rotation and hyperfine structure in the ground state of the molecular radical YbF using Doppler-free laser spectroscopy in a molecular beam. The spectrum reveals that the spin-rotation constant γ of the $X^2\Sigma^+$ ($\nu = 0$) state is exceptionally small. At the same time, the centrifugal distortion is so enormous that γ changes sign at rotational quantum number $N = 60$. To the best of our knowledge, this behavior is unprecedented.

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With its ionically bound closed-shell core and single valence electron, an alkaline earth monofluoride is the "alkali atom" of physical chemistry [1]. The ytterbium atom, having a filled f shell ($[\text{Xe}]4f^{14}6s^2$), resembles the alkaline earths. Thus, YbF should be rather similar to a heavy alkaline earth fluoride, although there might be complications associated with low-lying open f -shell configurations. Measurements of the YbF spectrum [2,3] have identified five electronic states and the $X^2\Sigma^+$ and $A^2\Pi$ states have been rotationally analyzed. These show that the gross features of YbF do indeed bear a striking resemblance to the structure of CaF, SrF, or BaF, although the spin-orbit interaction in YbF is much larger and some of its excited states are strongly perturbed. In this respect, YbF occupies a rather special position, more complicated than the simple alkaline earth fluorides, but simpler than the other lanthanide fluorides which have a large number of low-lying electronic states resulting from $4f$ superconfigurations [4]. YbF is also interesting from a completely different point of view. As a heavy, polar paramagnetic molecule, it is an extraordinarily sensitive system in which to detect an electric dipole moment of the electron [5] and hence to search for new interactions beyond the standard model of elementary particle physics.

In this Letter we focus on the spin-doubling and hyperfine interaction constants in the ground state of YbF, which we have measured using high-resolution laser-induced fluorescence spectra from a molecular beam crossed by a laser beam. This structure has not previously been resolved in optical spectra. Until now, the only information available came from a matrix isolation experiment [6] where g_{\perp} and g_{\parallel} of the gyromagnetic tensor and the magnitudes $|A_{\perp}|$ and $|A_{\parallel}|$ of the hyperfine tensor components were measured. These authors determined a value $\gamma = 102 \pm 10$ MHz for the spin-doubling constant by using the Curl equation $\gamma = -2B\Delta g_{\perp}$, which is typically accurate to 10% [7].

Table I summarizes the known spin-doubling and hyperfine constants for some $^2\Sigma^+$ molecules related to YbF and shows that the agreement between gas phase measurements and matrix isolation studies is quite good for these molecules. For YbF, however, we find that the spin doubling in the gas phase is an order of magnitude

smaller than the estimate based on the matrix-isolation data. Moreover, the centrifugal distortion is so enormous that γ changes sign as the molecular rotation increases (at $N \sim 60$). The small value of γ is quite unusual, while the observation of a sign change with rotation is, to the best of our knowledge, unprecedented.

We produce a molecular beam with a high YbF fraction by reducing YbF₃ with Al at about 1200 °C in a resistively heated oven. The mixture of YbF₃ and Al is sealed in a cylindrical stainless steel oven which has a 0.045" diameter aperture in one end cap to define the molecular beam. This is placed inside an alumina tube, around which we wrap approximately 2 m of 0.01" tungsten wire in a spiral groove. The assembly is surrounded by spun alumina insulation (Carborundum Fiberfrax) and packed into a water-cooled jacket. Typically, the heater dissipates 200 W to keep the oven at 1200 °C. We find that the YbF fraction of the beam depends strongly on temperature, increasing dramatically as the oven temperature rises from 1000° to 1200 °C.

For this experiment, we looked at the 0-0 band of the $A^2\Pi_{1/2}-X^2\Sigma^+$ transition, for which the bandhead is at 552.14 nm. The molecular beam was crossed at right angles by a 120 μW elliptical laser beam (3 mm \times 5 mm) produced by a single mode cw laser (Spectra Physics 380D using R110 dye). The laser-induced fluorescence was collected through $f = 1$ optics and was detected using a pulse-counting photomultiplier tube. We placed a 10 nm band pass interference filter (centered at 550 nm) in front of the tube in order to reduce the scattered blackbody radiation from the oven to an acceptable level. Rather than collimate the molecular beam, we controlled the Doppler width by introducing a narrow slit (1 mm \times 3 mm) in the image plane to define the region from which fluorescence was collected. About half the spectra were recorded at a distance of 21 cm from the oven, where the residual Doppler width was approximately 15 MHz, as measured using the intrinsically narrow $(6s^2)^1S_0-(6s6p)^3P_1$ atomic Yb line. The rest of the data were taken at a distance of 8 cm with a Doppler width of 32 MHz. The spectrum was highly congested because the P , Q , and R branches overlap and several vibrational levels were thermally populated in the beam.

TABLE I. Ground state properties of some $^2\Sigma$ fluorides. Quantities are in MHz except where noted.

	Gas phase parameters					Matrix isolation ^a			
	B_e (cm ⁻¹)	γ_0	γ_1 (Hz)	b	c	$-2B\Delta g_{\perp}$	b	c	
CaF	0.3437	39.66	10.26	109.2	40.12	39	106	43	Ref. [8]
SrF	0.2505	75.02	58.38	97.67	29.85	60	95	31	Ref. [15]
BaF	0.2165	80.92	112	63.51	8.22	78	59	8	Ref. [16]
YbF	0.2124	13.30	-3801	142	84	102	134	86	This work

^aRef. [7].

Moreover, Yb has five abundant isotopes (^{172}Yb , ^{174}Yb , and ^{176}Yb have nuclear spin $I = 0$, ^{171}Yb has $I = \frac{1}{2}$, and ^{173}Yb has $I = \frac{5}{2}$) which produce isotope shifts and hyperfine splittings in the range 1–10 GHz. Many of the small lines in the spectra of the odd isotopes were not clear enough to analyze.

In order to make a coarse identification of the lines, we scanned the region from the bandhead out to $Q(73)$, a range of ~ 1000 GHz, in sections of roughly 5 GHz. The absolute frequency of the laser was monitored using a wave meter accurate to 300 MHz, and relative frequencies were calibrated by means of a stable 10 cm confocal Fabry-Pérot cavity of low finesse. Once we had identified spectral features of interest for this study, we made narrower scans (~ 1 GHz) which were calibrated using a 50 cm Fabry-Pérot cavity. Figure 1(a) shows a scan through the $P(70)$ transition of ^{174}YbF . The solid line is a fit by the sum of four Lorentzians of equal width (15 MHz) and height. Figure 1(b) shows the $P(13)$ transition of ^{174}YbF , with a fit by four equal Lorentzians of 32 MHz width.

The structure of these spectra can be understood using the following effective Hamiltonian for the $X^2\Sigma^+$ ground state [1,7,8]:

$$H = \gamma \mathbf{S} \cdot \mathbf{N} + b \mathbf{I} \cdot \mathbf{S} + c I_z S_z, \quad (1)$$

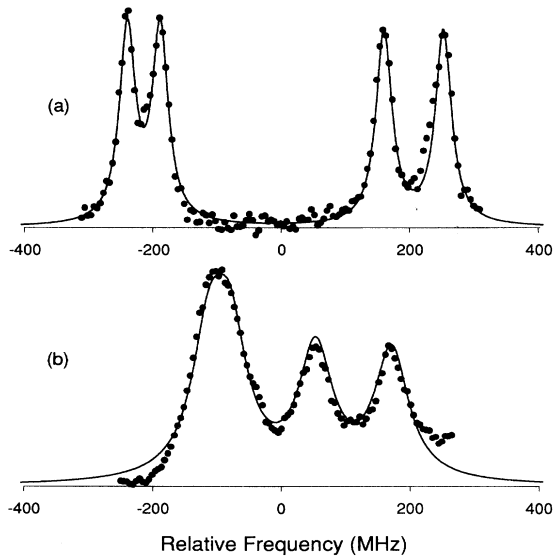
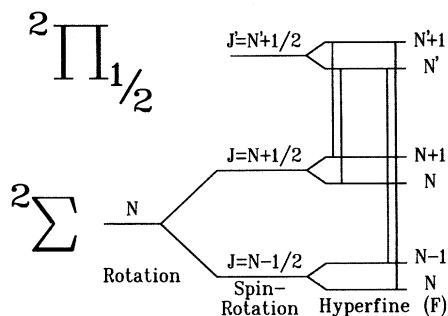


FIG. 1. Laser-induced spectra of ^{174}YbF $A^2\Pi_{1/2}-X^2\Sigma^+$. (a) $P(70)$. (b) $P(13)$. (●): Data. (—): Fit by sum of Lorentzians (see text).

where \mathbf{S} is the electron spin, \mathbf{N} is the rotational angular momentum, \mathbf{I} is the ^{19}F nuclear spin ($I = \frac{1}{2}$), and z components are along the internuclear axis. The ^{174}Yb nuclear spin is zero. In writing Eq. (1) we have ignored [9] a term of the form $C\mathbf{I} \cdot \mathbf{N}$, which is expected to be smaller than the above interactions by a factor on the order of the electron-mass/nuclear-mass ratio; for alkaline earths C is typically only a few tens of kHz. From the matrix isolation experiment of van Zee *et al.* [6], we already know that $|A_{\parallel}| = 220$ MHz and $|A_{\perp}| = 134$ MHz. Since $b = A_{\perp}$ and $c = A_{\parallel} - A_{\perp}$, there are four possible sets of values for b and c . Diagonalization of this Hamiltonian for a given N yields four states with total angular momenta $F = N + 1$, N , $N - 1$, and N . At a sufficiently large value of γN the spin-rotation interaction dominates, forming a spin doublet with intermediate angular momenta $J = N \pm \frac{1}{2}$, each of which is then doubled by the hyperfine interaction of the fluorine nucleus, as shown in Fig. 2. The four states so formed correspond to the four peaks shown in Fig. 1(a), where the 400 MHz splitting is due to the spin-doubling interaction, while the smaller intervals are the hyperfine doublets. At lower N , as in Fig. 1(b), the spin rotation and hyperfine interactions are comparable in magnitude and the intermediate quantum number, J is no longer a good one. In the $A^2\Pi_{1/2}$ upper level, the large fine structure interaction gives rise to levels of angular momentum $J' = N' + \frac{1}{2}$, as shown in Fig. 2. (These are Λ doubled, but the parity selection rule chooses only one member of the Λ doublet in a given line of our spectrum.) Each level is split by the much weaker fluorine hyperfine interaction to form a hyperfine doublet of total angular momentum $F' = N' + 1$ and $F' = N'$. Thus one Q -branch line ($N' = N$) consists of seven allowed $\Delta F = 0, \pm 1$ transitions. For sufficiently large N , there is a quasiselection rule $\Delta F = \Delta J$, which reduces the number of transitions in the line from seven to four, as illustrated in Fig. 2. The P -branch line similarly consists of just four transitions.

Altogether, we measured and analyzed 10 Q -branch and 21 P -branch spectra similar to those shown in Fig. 1, and from each data set we determined four line centers to be compared with the eigenvalues of Eq. (1). Only one of the four possibilities for b and c is compatible with our results, namely, $b = 134$ MHz and $c = 86$ MHz. With these values, we were able to fit the four centers separately for each rotational transition to determine $\gamma(N)$, the fitting parameters being γ and the zero of energy for each spectrum. The results, plotted in Fig. 3, show

FIG. 2. Allowed ${}^2\Pi_{1/2}$ - ${}^2\Sigma^+$ hyperfine transitions.

that $\gamma(N)$ is very well described by the usual form $\gamma_0 + \gamma_1 N(N+1)$. A least-squares fit yielded the values (with 1σ uncertainties)

$$\begin{aligned}\gamma_0 &= 13.44(6) \text{ MHz}, \\ \gamma_1 &= -3.842(14) \times 10^{-3} \text{ MHz}.\end{aligned}\quad (2)$$

It should be noted that in obtaining these values we have assumed that the gas phase and matrix isolation hyperfine constants are the same and we have neglected the hyperfine splitting of the upper level. The main point here is the demonstration that $\gamma(N)$ varies linearly with $N(N+1)$ and has a very large slope.

In order to make a more complete analysis of our data, we computed the eigenvalues [8] of Eq. (1) with $\gamma(N)$ explicitly constrained to the form $\gamma_0 + \gamma_1 N(N+1)$ and made a global fit, varying γ_0 , γ_1 , b , c , and the zero of energy in each spectrum. We also included the effect of a nonzero hyperfine splitting δ of the upper level. The result is shown in Fig. 4 where the points are the centers of the four lines in each spectrum and the solid lines are the best fit by the eigenvalues of Eq. (1). The results of this analysis are (with 1σ uncertainties)

$$\begin{aligned}\gamma_0 &= 13.31(8) \text{ MHz}, \quad \gamma_1 = -3.801(15) \times 10^{-3} \text{ MHz}, \\ b &= 142(2) \text{ MHz}, \quad c = 84(8) \text{ MHz}, \\ \delta &= 2.8(1.8) \text{ MHz}.\end{aligned}\quad (3)$$

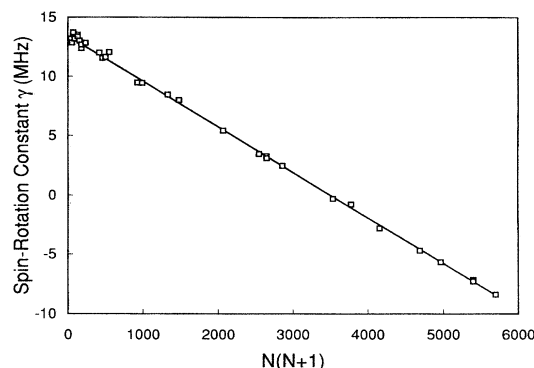
$$\gamma_0 \approx \sum_{n,\nu} \frac{\langle X^2\Sigma^+ | B(r)L^- | n^2\Pi_{1/2}, \nu \rangle \langle n^2\Pi_{1/2}, \nu | A(r)L^+ | X^2\Sigma^+ \rangle}{E(n^2\Pi_{1/2}, \nu) - E(X^2\Sigma^+)} + \text{H.c.}, \quad (4)$$

where n and ν indicate the configuration and vibrational excitation of the intermediate state, and H.c. is the Hermitian conjugate.

We are able to make a rough estimate of γ_0 on the basis of this equation if we suppose that the perturbation is due mainly to the A state. First, we approximate the X state by a combination of singly occupied σ orbitals

$$|X\rangle = x_s|6s\sigma\rangle + x_p|6p\sigma\rangle + x_d|5d\sigma\rangle + \dots, \quad (5)$$

with coefficients [11] $|x_s|^2 = 0.84$, $|x_p|^2 = 0.15$, and $|x_d|^2 \approx 0$. Similarly, for the $A^2\Pi_{1/2}$ state we write

FIG. 3. (\square): γ for each rotational transition with b and c held constant (see text). (—): fit by $\gamma(N) = \gamma_0 + \gamma_1 N(N+1)$.

The hyperfine constant b disagrees slightly with the matrix isolation value (134 MHz), but no more than is typical when comparing matrix isolation and gas phase data [7]. There is no significant disagreement in the value of c . Our value for δ does little more than place an upper limit of about 5 MHz on the hyperfine splitting of the ${}^2\Pi_{1/2}$ levels. The results of primary interest are γ_0 and γ_1 , both of which are anomalous.

As discussed elsewhere [8,10], γ_0 can be viewed as resulting from two distinct mechanisms. The more obvious one, the interaction of the electron spin with the magnetic field produced by the rotation of the molecular framework, typically contributes only a few MHz and could not be expected to make a significant contribution here. The second mechanism, normally the dominant one, is more complicated. The X state is perturbed by ${}^2\Pi_{1/2}$ terms, both through the L -uncoupling interaction $-2B\mathbf{J} \cdot \mathbf{L}$ [10] and through the spin-orbit interaction. The off-diagonal matrix element of the former interaction is different for the two degenerate states e ($J = N + 1/2$) and f ($J = N - 1/2$) of a given rotational level N , while the spin-orbit interaction is much stronger and perturbs them equally. Thus the splitting of the e and f states appears in second order as an interference between the two perturbations

$$|A\rangle = a_p|6p\pi\rangle + a_d|5d\pi\rangle + \dots, \quad (6)$$

where the coefficients can be estimated from known fine structures as follows [2]. We take the fine structure interaction to be $\zeta_{n,l}\mathbf{l} \cdot \mathbf{s}$ and use the values $\zeta_{6p} = 2220 \text{ cm}^{-1}$ and $\zeta_{5d} = 549 \text{ cm}^{-1}$, which are those of the Yb⁺ ion. Knowing that the fine structure interval in the A state of YbF is 1365 cm^{-1} , we infer the values $|a_p|^2 = 0.49$, $|a_d|^2 = 0.51$. Neglecting all other states, and taking the vibrational overlap integrals to be unity,

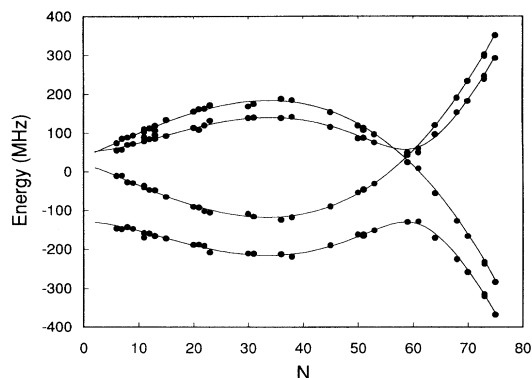


FIG. 4. (●): Centers of hyperfine lines. (—): Fit by the eigenvalues of Eq. (1), with γ of the form $\gamma(N) = \gamma_0 + \gamma_1 N(N + 1)$.

we obtain

$$\gamma_0 \approx 4 \frac{|a_p|^2 |x_p|^2 \zeta_{6p} B}{E(A_1) - E(X)} = 270 \text{ MHz}. \quad (7)$$

In the alkaline earth fluorides this kind of estimate is reliable to better than 40%, while for YbF it is actually larger than our measured value by a factor of 20. The inclusion of more single-electron $^2\Pi_{1/2}$ states will not improve the agreement, since all the factors involved are positive. A reduction of γ_0 could occur through interference between the contributions of p and d orbitals, but in our case x_d is too small for any strong reduction to be possible [12]. We are therefore led to believe that the small value of γ_0 indicates the presence of a more complicated $^2\Pi_{1/2}$ state, perhaps involving an excitation out of the $4f$ shell, which largely cancels the effect of the A state [13]. Such $4f$ -excited states have been predicted [11] in YbF, but have not yet been observed. The YbF $A^2\Pi_{1/2}$ state is known to be strongly perturbed vibrationally, but the perturbing state(s) have not been identified.

The situation for γ_1 is if anything less clear. Veseth [14] discussed the centrifugal distortion of γ , but in its simplest form [Eq. (34) of [14]] the theory does not even predict the correct sign of γ_1 for the alkaline earth fluorides. For these molecules the excited state structure is well understood, but to our knowledge there has been no quantitative explanation of γ_1 for any of them. For YbF, where our information on the excited state structure is still fragmentary, quantitative calculation seems impossible. Qualitatively, the large size of γ_1 we find in YbF implies an interaction between the ground state and a state with a very different potential surface. The dominant contribution to γ_1 is unlikely to come from the A state.

Although we do not know the cause of the anomalous sizes of γ_0 and γ_1 , it is clear that a special set of circumstances is required. One obvious hypothesis is that both the ground state and the excited state A have substantial f character, but this seems to be inconsistent

with the calculations of Dolg, Stoll, and Preuss [11]. This puzzle may not be solved until more detailed information is known about the wave functions of the ground and low-lying excited states. The anomalous spin-rotation interaction we have observed provides a strong impetus for further study of this problem.

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