Field-free, Stark, and Zeeman spectroscopy of the $\tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ transition of ytterbium monohydroxide

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The $0_0^0 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$, $1_1^0 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$, and $1_0^1 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$ bands of an internally cold molecular beam sample of ytterbium monohydroxide, YbOH, have been recorded at the near natural linewidth limit and analyzed to determine the fine structure parameters. Numerous lines in the $0_0^0 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$ band associated with the lowest rotational levels were recorded in the presence of a static electric field and analyzed to determine the magnitude of the molecular frame permanent electric dipole moment, $|\vec{\mu}_{el}|$, for the $\tilde{X} \, {}^2 \Sigma^+(0, 0, 0)$ and $\tilde{A} \, {}^2 \Pi_{1/2}(0, 0, 0)$ states of 1.9(2) and 0.43(10) D, respectively. An electrostatic polarizability model is used to predict the $\vec{\mu}_{el}$ for the $\tilde{X} \, {}^2 \Sigma^+(0, 0, 0)$ state. The $0_0^0 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$ band is recorded in the presence of a weak static magnetic field to observe the electric dipole allowed transitions having $\Delta J = -2$, which are used to assist in the rotational quantum number assignment and confirm the identity of the excited state. An expression for the $\tilde{A} \, {}^2 \Pi_{1/2}(0, 0, 0)$ magnetic *g* factor is derived and shown to correctly model the observed magnetic tuning. A comparison with YbF is made and implications for the use of YbOH as a venue for symmetry violation measurements are discussed.

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I. INTRODUCTION

The linear triatomic molecule YbOH may be a sensitive venue measuring the electron electric dipole moment (eEDM) and/or nuclear magnetic quadrupole moment (MOM) [1]. Traditionally, open shell states of the diatomic molecules such as YbF [2-5], ThO [6], and HfF⁺ (Ref. [7]) have been venues for attempts to measure an eEDM. Recent efforts to improve the sensitivity of eEDM measurements include increasing the coherence time by laser cooling [5] the sample and increasing the internal effective electric field [8], E^{eff} , either by increasing the polarization caused by the application of an external static electric field and/or selecting a molecule with intrinsically large enhancements. As noted by Kozyryev and Hutzler [1], YbOH has both an electronic structure amenable to laser cooling, and low-lying bending modes with closely spaced states of opposite parity which should enable near full polarization with application of a modest external static electric field. The laser cooling and trapping scheme experimentally demonstrated with SrOH [9] is also feasible for YbOH. Although the metastable bending mode, $\tilde{X}^{2}\Sigma^{+}(0, 1^{1}, 0)$, is most desirable for parity violation measurements because of the ease of polarization, the $\tilde{X}^{2}\Sigma^{+}(0,0,0)$ state may also be advantageous compared to the currently used $X^{2}\Sigma^{+}(v=0)$ state of YbF because of the much smaller proton hyperfine splitting compared to that from ¹⁹F. Here we report the determination ground and excited state energies and molecular frame electric and magnetic dipole moments which are requisite for the proposed laser cooling and subsequent EDM measurements.

The Yb-O stretching, Yb-O-H bending, and O-H stretching modes of this linear molecule will be labeled as ν_1 , ν_2 , and ν_3 , respectively. The 000-000 fundamental band, 100-000, and 000-100 bands involving one quanta Yb-O stretching of the $\tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$ electronic transition studied here will, for convenience, be designated as $0_0^0 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$, $1_0^1 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$, and $1_1^0 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$, and are near 577, 558, and 595 nm, respectively. Although the low-*J* branch features of the $0_0^0 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$ band are of primary interest for laser cooling, transitions associated with the $1_0^1 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$ bands will be used for monitoring and repumping [9].

Previous optical spectroscopic studies of gas-phase YbOH are limited to the high-temperature, Doppler limited study of various bands of the $\tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ and $\tilde{A}^2 \Pi_{3/2} \tilde{X}^{2}\Sigma^{+}$ electronic transitions [10]. In that study, the lowresolution laser excitation spectrum in the 510-600 nm range was recorded using broadband fluorescence detection. The Doppler limited laser excitation spectra of the $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ and $1_1^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ bands were recorded and analyzed to produce fine structure parameters for the ¹⁷⁴YbOH and ¹⁷²YbOH isotopologues. The data set consisted primarily of spectral features associated with high rotational states and not those relevant to laser cooling and EDM measurements. A v_1 vibrational spacing for the $\tilde{X}^2 \Sigma^+$ state of 529.341(1) cm⁻¹ was obtained from the determined origins of the $0_0^0 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ and $1_1^0 \tilde{A}^2 \Pi_{1/2} \tilde{X}^2 \Sigma^+$ bands. Dispersed fluorescence spectra resulting from broadband dye laser excitation were analyzed to determine the ν_2 vibrational spacing for the $\tilde{X}^2 \Sigma^+$ state of 339(5) cm⁻¹. The observed transition wave numbers for numerous other band heads in the low-resolution excitation

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spectra were analyzed to determine ν_1 and ν_2 vibrational spacing for the $\tilde{A} \,{}^2\Pi_{1/2}$ state of 573(5)cm⁻¹ and 357(5)cm⁻¹, respectively. The spacing between the $0_0^0 \tilde{A} \,{}^2\Pi_{1/2} - \tilde{X} \,{}^2\Sigma^+$ and $0_0^0 \tilde{A} \,{}^2\Pi_{3/2} - \tilde{X} \,{}^2\Sigma^+$ bands gave an estimate for the spinorbit splitting of 1350 cm⁻¹.

We recently reported on the rotational spectroscopy of ¹⁷⁴YbOH recorded using a separated field pump-probe microwave optical double resonance (PPMODR) scheme [11]. In that study, 18 lines associated with the $N = 3 \rightarrow$ 4, $4 \rightarrow 5$, $5 \rightarrow 6$, and $6 \rightarrow 7$ pure rotational transitions were recorded and analyzed to precisely determine the fine and proton magnetic hyperfine parameters for the $\tilde{X}^{2}\Sigma^{+}(0,0,0)$ state. The precise determination of the $\tilde{X}^{2}\Sigma^{+}(0, 0, 0)$ eigenvalues and eigenvectors greatly facilitated the present analysis. A partial analysis of the optical spectra reported here was performed in order to identify the appropriate transitions required for the pump and probe laser scheme used in the PPMODR measurements. In addition, the improved set of field-free parameters resulting from the optical analysis described here was used to predict the approximate rotational transition frequencies.

II. EXPERIMENT

The production of a cold molecular beam sample of YbOH was identical to that used previously in the PPMODR measurement [11]. Specifically, a Yb rod was ablated (20 Hz, 532 nm, ~ 10 mJ/pulse) in the presence of a methanol-argon expansion and the expansion skimmed to produce a well collimated beam. Each ablation pulse produces an approximately 40- μ s pulse of molecules at the detection region. The methanol-argon mixture was achieved by flowing argon over a container filled with liquid methanol maintained at room temperature. A relatively low concentration ($\sim 0.25\%$) of methanol is used, given the room temperature vapor pressure of methanol (~10 kPa) together with the employed relatively high backing pressure of argon (~4000 kPa). The production of YbOH was approximately a factor of 4 lower when a 50% hydrogen peroxide solution was substituted for methanol. The molecular beam was probed at approximately 0.5 m from the source with the output of a single frequency, unfocussed (diameter \sim 5 mm) dye laser and the resulting laser-induced fluorescence (LIF) signal was viewed through a bandpass filter. The $\tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ transitions are very diagonal (i.e., $\Delta v = 0$). Hence, while relatively low laser power (~5 mW) was used for the more intense $0_0^0 \tilde{A} \,^2 \Pi_{1/2}$ – $\tilde{X}^2 \Sigma^+$ band, higher power (~20 mW) was used for the weaker $1_0^1 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ and $1_0^1 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ bands. The $0_0^0 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ and $1_1^0 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ transitions were detected by monitoring the $\tilde{A}~^2\Pi_{1/2}(0,0,0) \rightarrow$ $\tilde{X}^{2}\Sigma^{+}(0, 0, 0)$ emission through a 580 ± 10 nm bandpass filter. The $1_0^1 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ transition was detected by monitoring the off-resonance $\tilde{A}^2 \Pi_{1/2}(1,0,0) \rightarrow \tilde{X}^2 \Sigma^+(1,0,0)$ emission viewed also through a 580 ± 10 nm bandpass filter. The signal was processed using gated photon counting. Typically, the photon counts of 30 laser ablation pulses were summed at a given cw-dye laser excitation wavelength. Absolute wavelength was determined by corecording the sub-Doppler I_2 spectrum [12]. The relative wavelength was more

precisely measured by corecording the transmissions of an actively stabilized étalon (free spectra range = 751.393 MHz).

The experimental arrangement for the optical Stark measurements has been described previously [13]. The systematic error associated with the mechanical measurement of the Stark plate spacing (nominally 2 cm) and the voltage (typically 2 kV) is estimated to be less than 2%. Observation of Zeeman-induced optical transitions was also utilized for confirming the rotational quantum number assignment and elucidating the nature of the excited electronic state (see below). The experimental setup for the optical Zeeman measurements has also been described previously [14]. A relatively weak (<100 G), tunable static magnetic field was generated by a C-frame, fixed gap dipole electromagnet. The molecular beam passed through 5-mm holes drilled in the poles of the dipole electromagnet. A polarization rotator was used to control the relative orientation of the linearly polarized laser radiation to the static electric or magnetic fields.

III. OBSERVATIONS

The laser excitation spectrum in the region of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band head is presented in Fig. 1. Also shown in Fig. 1 are the assignment and stick spectra associated with the ¹⁷⁴YbOH and ¹⁷²YbOH isotopologues obtained using a rotational temperature of 20 K and the optimized parameters (*infra vide*). The $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band is highly congested because the spectral shifts for the numerous isotopologues [170 Yb(3.5%), 171 Yb(14.3%), 172 Yb(21.9%), 173 Yb(16.1%), 174 Yb(31.8%), and 176 Yb(12.7%)] are small owing to similar potential energy surfaces of the $\tilde{A}^2 \Pi_{1/2}$ and $\tilde{X} {}^{2}\Sigma^{+}$ states. Spectral features for the three most abundant even isotopologues, 172 YbOH, 174 YbOH, and 176 YbOH, could be assigned. Spectral feature of the odd isotopologues, ¹⁷³YbOH and ¹⁷¹YbOH, are not readily assigned because of the large 171 Yb(I = 1/2) and 173 Yb(I = 5/2) hyperfine splitting. No H(I = 1/2) splitting is observed and a traditional ² Π [Hund's case (a)]- ${}^{2}\Sigma^{+}$ [Hund's case (b)] branch designation, $\Delta N \Delta J_{F'_i F''_i}(N'')$, is used for labeling the transitions associated with the even Yb(I = 0)OH isotopologues. Note that for the $\tilde{X}^{2}\Sigma^{+}(\nu_{1}, 0, 0)$ states $F_{i}^{"} = 1$ and 2 for $J^{"} = N^{"} + 1/2$ and J'' = N'' - 1/2, respectively, and all levels associated with the $\tilde{A}^2 \Pi_{1/2}(\nu_1, 0, 0)$ states have $F'_i = 1$. The band head region (see Fig. 1) consists of low-*J* features of the ${}^{P}P_{11}$, ${}^{Q}Q_{11}$, ${}^{P}Q_{12}$, and ${}^{Q}R_{12}$ branches. The ${}^{O}P_{12}$ branch features are relatively unblended and are to the red side of the band head while the ${}^{R}R_{11}$ lines are mostly unblended and to the blue side of the band head region presented in Fig. 1. The 66 and 61 measured optical transition wave numbers for the ¹⁷⁴YbOH and ¹⁷²YbOH isotopologues are presented in Tables I and II, respectively. Also given are the assignments and difference between the observed and calculated values.

The laser excitation spectrum in the region of the $1_1^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band head is presented in Fig. 2 along with the assignment and stick spectrum associated with ¹⁷⁴YbOH. The signal-to-noise ratio for this band is significantly lower than that of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band because of the relatively low population of the excited $\tilde{X} \,^2 \Sigma^+(1,0,0)$ state and the smaller Franck-Condon factor. The larger vibrational isotopic shifts of the $\tilde{X} \,^2 \Sigma^+(1,0,0)$



FIG. 1. The laser excitation spectrum in the region of the $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ band head of YbOH. The assignment and stick spectra associated with the ¹⁷⁴YbOH and ¹⁷²YbOH isotopologues were obtained using a rotational temperature of 20 K and the optimized parameters.

state relative to the $\tilde{X} {}^{2}\Sigma^{+}(0, 0, 0)$ state cause the features of the various isotopologues to be less overlapped for the $1_{1}^{0}\tilde{A} {}^{2}\Pi_{1/2} - \tilde{X} {}^{2}\Sigma^{+}$ band (Fig. 2) as compared to the $0_{0}^{0}\tilde{A} {}^{2}\Pi_{1/2} - \tilde{X} {}^{2}\Sigma^{+}$ (Fig. 1) band. The 40 measured optical transition wave numbers for the 174 YbOH isotopologue are presented in Table III along with assignments and differences between the observed and calculated values.

The laser excitation spectrum in the region of the $1_0^1 \tilde{A} \, {}^2 \Pi_{1/2} - \tilde{X} \, {}^2 \Sigma^+$ band head is presented in Fig. 3 along with the assignment and stick spectrum associated with the ¹⁷⁴YbOH. The signal-to-noise for this band is comparable to that of the $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ band because although the Franck-Condon factor is much smaller, higher laser power could be used because the off-resonant fluorescence detection. The branch ordering is unusual for the $1_0^1 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band because the Λ -doubling parameters, p + 2q, in the $\tilde{A}^2 \Pi_{1/2}(1,0,0)$ state are greater than twice the rotational parameter, 2B. This causes the ${}^{P}P_{11}$ and ${}^{P}Q_{12}$ branch features to appear at higher transition wave numbers than the $^{Q}Q_{11}$ and ${}^{Q}R_{12}$ branch features. The larger vibrational isotope shift of the $\tilde{A}^2 \Pi_{1/2}(1, 0, 0)$ state relative to the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ state causes the features of the various isotopologues to be less overlapped for the $1_0^1 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band as compared to the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band. The 66 measured optical transition wave numbers for the ¹⁷⁴YbOH isotopologue are presented in Table IV along with assignments and differences between the observed and calculated values.

 $^{O}P_{12}(2) (\nu = 17322.1467 \,\mathrm{cm}^{-1}),$ ${}^{Q}Q_{11}(0)(v =$ The 17323.6214 cm⁻¹), and ${}^{R}R_{11}(0)(\nu = 17325.0365 \text{ cm}^{-1})$ lines of the ¹⁷⁴YbOH isotopologue of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band were selected for Stark measurements because these features are relatively unblended and associated with low-J energy levels. The field-free and Stark spectra for the ${}^{R}R_{11}(0)$ line with parallel polarization ($\Delta M_J = 0$) are given in Fig. 4. Also presented are the assignment and a plot of the energy levels as a function of external electric field strength. The shift of the ${}^{R}R_{11}(0)$ line is primarily due to the second-order Stark shift of the N = 0, J = 1/2, "+ parity" level of the $\tilde{X}^2 \Sigma^+(0,0,0)$ state caused by interaction with the N = 1, J = 3/2 ($E = 0.4889 \text{ cm}^{-1}$) and N = 1, J = 1/2 $(E = 0.4929 \text{ cm}^{-1})$ "- parity" levels. The $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ excited state level is relatively insensitive to the electric field because of the large Λ doubling and, as it turns out, this state has a small molecular frame electric dipole moment, $\vec{\mu}_{el}$. Specifically, the J = 3/2 parity level, which is the upper energy terminus of the ${}^{R}R_{11}(0)$ line, is 0.876 cm⁻¹ higher in energy than the J = 3/2 + parity component. The eight measured Stark shifts, assignments, and differences between the observed and calculated shifts are given in Table V.

The predicted optical spectrum based upon the published spectroscopic parameters [10], which were obtained from analysis of high-J rotational levels, did not reproduce the observed spectrum of Figs. 1–3, which are associated with low-J rotational levels. Combination differences

Lines	<i>N</i> ″′	J'	Observed	Obs-Calc	Lines	$N^{\prime\prime}$	J'	Observed	Obs-Calc
$\overline{\mathcal{Q}}_{R_{12}}$	1	3/2	17323.6687	0.0001	${}^{R}R_{11}$	0	3/2	17325.0365	-0.0011
	2	5/2	17323.7323	-0.0005		1	5/2	17326.0323	-0.0004
	3	7/2	17323.8126	-0.0002		2	7/2	17327.0432	-0.0004
	4	9/2	17323.9091	0.0005		3	9/2	17328.0703	0.0003
	5	11/2	17324.0200	-0.0002		5	13/2	17330.1703	0.0001
	6	13/2	17324.1480	0.0004		6	15/2	17331.2434	-0.0003
	7	15/2	17324.2918	0.0009		7	17/5	17332.3326	-0.0003
	8	17/2	17324.4499	0.0000		8	19/2	17333.4377	0.0002
	9	19/2	17324.6250	0.0002	${}^{P}P_{11}$	1	1/2	17323.5699	-0.0008
	10	21/2	17324.8150	-0.0006		2	3/2	17323.5699	0.0003
	11	23/2	17325.0228	0.0007		3	5/2	17323.5845	0.0002
${}^{P}Q_{12}$	1	1/2	17323.5669	0.0003		4	7/2	17323.6148	0.0001
	2	3/2	17323.5622	-0.0007		5	9/2	17323.6610	0.0001
	3	5/2	17323.5754	0.0005		6	11/2	17323.7225	-0.0003
	4	7/2	17323.6028	0.0002		7	13/2	17323.8006	0.0003
	5	9/2	17323.6462	0.0001		8	15/2	17323.8939	0.0003
	6	11/2	17323.7052	-0.0001		9	17/2	17324.0026	0.0000
	7	13/2	17323.7803	0.0001		10	19/2	17324.1272	0.0001
	8	15/2	17323.8708	0.0000		11	21/2	17324.2670	-0.0006
	9	17/2	17323.9768	-0.0003		12	23/2	17324.4230	-0.0005
	10	19/2	17324.0991	0.0000	${}^{Q}Q_{11}$	0	1/2	17323.6214	-0.0001
	11	21/2	17324.2371	0.0004		1	3/2	17323.6728	0.0002
	12	23/2	17324.3901	0.0001		2	5/2	17323.7400	0.0005
${}^{O}P_{12}$	2	1/2	17322.1467	-0.0001		3	7/2	17323.8220	-0.0002
	3	3/2	17321.2146	-0.0001		4	9/2	17323.9212	0.0005
	4	5/2	17320.2987	0.0002		5	11/2	17324.0356	0.0006
	5	7/2	17319.3978	-0.0003		6	13/2	17324.1654	0.0003
	6	9/2	17318.5132	-0.0004		7	15/2	17324.3119	0.0009
	7	11/2	17317.6449	-0.0000		8	17/2	17324.4737	0.0009
	8	13/2	17316.7912	-0.0009		9	19/2	17324.6505	0.0001
	10	17/2	17315.1341	-0.0002		10	21/2	17324.8437	0.0000
${}^{O}O_{11}{}^{a}$	3	3/2	17321.2239	-0.0003		11	23/2	17325.0525	-0.0005
	4	5/2	17320.3108	0.0001					
	6	9/2	17318.5300	-0.0012					

TABLE I. Observed and calculated line positions in wave number (cm⁻¹) of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band system of ¹⁷⁴YbOH.

 ${}^{a O}O_{11}$ lines were induced by a magnetic field.

suggested that the previously determined spin-rotation parameter, γ , for the $\tilde{X}^{2}\Sigma^{+}(0, 0, 0)$ state was erroneous. To determine the spin-rotation splitting (i.e., the ρ doubling) of the $\tilde{X}^{2}\Sigma^{+}(0,0,0)$ state, a weak static magnetic field was used to mix states of the same parity in the $\tilde{X}^{2}\Sigma^{+}(0, 0, 0)$ state to observe electric dipole allowed optical transition having $\Delta J =$ -2. Specifically, magnetically induced transitions in the region of the ${}^{O}P_{12}(3)$ ($\nu = 17321.2146 \,\mathrm{cm}^{-1}$), ${}^{O}P_{12}(4)$ ($\nu =$ 17320.2987 cm⁻¹), and ${}^{O}P_{12}(6)$ ($\nu = 17318.5132$ cm⁻¹) lines of the $0_0^0 \tilde{A} \ ^2 \Pi_{1/2} - \tilde{X} \ ^2 \Sigma^+$ band were recorded. These transitions are associated with the $F_i'' = 2$ spin component of a given rotational level in the $\tilde{X} \,^2 \Sigma^+(0, 0, 0)$ state. The fieldfree and optical Zeeman spectra in the vicinity of the $^{O}P_{12}(3)$ line recorded at a field of 64 G with parallel polarization $(\Delta M_J = 0)$ are presented in Fig. 5. Also presented are the assignment, predicted spectrum, and energy level tuning for the ¹⁷⁴YbOH isotopologue. The predicted spectrum of Fig. 5 was obtained using a narrower linewidth than that of the observed spectrum (10 MHz vs 30 MHz) to emphasize the underlying structure. The induced transition has $\Delta N = \Delta J = -2$ and originates from the $F_i'' = 1$ spin component corresponding to

a branch designation of $^{O}O_{11}$. Note that the effective g_J factor for the ground and excited state levels of the $^{O}O_{11}(3)$ line are of the same magnitude and sign resulting in a sharp spectral feature whereas those for the ${}^{O}P_{12}(3)$ line are of the same magnitude but opposite sign resulting in a broad, partially resolved spectral feature. The induced transition appears at 0.0093 cm⁻¹ higher than the $^{O}P_{12}(3)$ line which corresponds to $\gamma \approx -0.0027 \text{ cm}^{-1} [\Delta E(\rho \text{ doubling}) = \gamma (N + 1/2)]$, which is almost three times the previously determined [10] value and of opposite sign. With this value and the previously determined parameters [10] the ¹⁷⁴YbOH and ¹⁷²YbOH spectra could be assigned. The transition wave numbers for the $^{O}O_{11}$ lines are given in Table I. It is important to note that the characterization of the optical spectrum described here was performed prior to the microwave measurements [11] and was essential for estimating the pure rotational transition frequencies. A recent reanalysis [15] of the high-J data given in Ref. [10], involving a rearrangement of the ${}^{Q}Q_{11}$ and ${}^{S}R_{12}$ branch and isotopologue assignments in the 000-000 origin band, yielded a value of γ in good agreement with the present value.

Lines ^a	<i>N</i> ″′	J′	Observed	Obs-calc	Lines	<i>N</i> ″′	J'	Observed	Obs-calc
$Q_{R_{12}}$	1	3/2	17323.6965	-0.0002	${}^{R}R_{11}$	0	3/2	17325.0673	0.0002
	2	5/2	17323.7613	0.0003		1	5/2	17326.0635	0.0002
	3	7/2	17323.8409	-0.0002		2	7/2	17327.0747	-0.0005
	4	11/2	17323.9368	-0.0002		3	9/2	17328.1023	-0.0006
	5	13/2	17324.0487	0.0000		5	13/2	17330.2048	-0.0004
	6	15/2	17324.1763	0.0000		6	15/2	17331.2789	-0.0010
	7	17/2	17324.3199	0.0003		7	17/5	17332.3714	0.0012
	8	19/2	17324.4788	-0.0001		8	19/2	17333.4762	0.0001
	9	21/2	17324.6537	-0.0002	$^{\mathcal{Q}}Q_{11}$	0	1/2	17323.6500	0.0004
*	10	23/2	17324.8449	0.0001		1	3/2	17323.7003	-0.0005
	11	25/2	17325.0518	0.0002		2	5/2	17323.7678	0.0001
${}^{P}Q_{12}$	1	1/2	17323.5952	0.0006		3	7/2	17323.8504	-0.0001
	2	3/2	17323.5910	0.0002		4	9/2	17323.9485	-0.0006
*	3	5/2	17323.6028	0.0001		5	11/2	17324.0636	0.0000
	4	7/2	17323.6309	0.0005		6	13/2	17324.1942	0.0004
*	5	9/2	17323.6734	-0.0005		7	15/2	17324.3403	0.0004
*	6	11/2	17323.7339	0.0008		8	17/2	17324.5020	0.0002
	7	13/2	17323.8084	0.0003		9	19/2	17324.6794	-0.0002
	8	15/2	17323.8989	0.0001		10	21/2	17324.8730	-0.0002
	9	17/2	17324.0044	-0.0008		11	23/2	17325.0828	0.0001
*	10	19/2	17324.1272	-0.0001	${}^{P}P_{11}$	3	3/2	17323.5976	0.0001
	12	23/2	17324.4189	0.0002		4	5/2	17323.6126	0.0004
$^{O}P_{12}$	2	1/2	17322.1732	0.0000		5	7/2	17323.6429	0.0003
	3	3/2	17321.2389	-0.0012		6	9/2	17323.6890	0.0002
	4	5/2	17320.3230	0.0001		7	11/2	17323.7508	0.0001
	5	7/2	17319.4219	0.0003		8	13/2	17323.8291	0.0007
	6	9/2	17318.5362	0.0001	*	9	15/2	17323.9212	-0.0006
	7	11/2	17317.6665	0.0000		10	17/2	17324.0305	-0.0004
	10	17/2	17315.1531	0.0001		11	19/2	17324.1555	-0.0002
	11	19/2	17314.3468	-0.0003		12	21/2	17324.2964	0.0001
		Std. dev. of	fit: 0.00042 cm^{-1}			13	23/2	17324.4527	0.0002

TABLE II. Observed and calculated line positions in wave number (cm⁻¹) of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band system of ¹⁷²YbOH.

^aLines marked with (*) are overlapped with ¹⁷⁴YbOH.

IV. ANALYSIS

The spectra were modeled using a standard effective Hamiltonian [16] that included the rotation (B and D) and spin-rotation (γ) terms for the $\tilde{X}^2 \Sigma^+$ state and the origin $(T_{\nu'\nu'})$, spin-orbit (A), rotation (B and D), and A-doubling (p+2q) terms for the $\tilde{A}^2 \Pi_{1/2}$ states. The spin-orbit parameter was constrained to the previously estimated value [10] of 1350 cm⁻¹. The parameters for the $\tilde{X}^2 \Sigma^+(0,0,0)$ state of ¹⁷⁴YbOH were constrained to those derived from the analysis of the rotational spectrum [11]. The centrifugal distortion parameters, *D*, for $\tilde{X}^2 \Sigma^+(1, 0, 0)(^{174}$ YbOH), $\tilde{X}^{2}\Sigma^{+}(0, 0, 0)(^{172}$ YbOH), $\tilde{A}^{2}\Pi_{1/2}(0, 0, 0)(^{174}$ YbOH), and $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)(^{172}$ YbOH) were constrained to the values obtained from the analysis of the high-temperature sample [10]. The *D* value for $\tilde{A}^2 \Pi_{1/2}(1, 0, 0)(^{174}$ YbOH) was fixed to a value extrapolated from the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)(^{174}\text{YbOH})$ value based upon the observed vibrational dependence of the $\tilde{X}^2 \Sigma^+$ state. In the field-free analysis, the eigenvalues and eigenvectors were obtained by diagonalization of 2×2 and 4 \times 4 matrices constructed in a Hund's case (a) basis ($\psi^{\text{basis}} = |\Lambda; S, \Sigma; J, \Omega, M_J\rangle$) for the $\tilde{X}^2 \Sigma^+$ and $\tilde{A}^2 \Pi_{1/2}$

states, respectively. A nonlinear least squares fitting procedure was used to obtain optimized parameters given in Table VI. The $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ and $1_1^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ measurements for 174 YbOH, which are given in Tables I and III, respectively, were combined in a single fit. The $1_0^1 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ field-free measurements for 174 YbOH given in Table IV and those for $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ measurements for 172 YbOH given in Table II were fit independently. The determined parameters and associated errors are given in Table VI.

The effect of the static electric field was modeled by adding the operator:

$$\hat{H}^{\text{Stark}} = -\hat{\mu}_{el} \cdot \hat{E}.$$
 (1)

The eigenvalues and eigenvectors were obtained by diagonalizing 8×8 and 16×16 matrices constructed in a Hund's case (a) basis set for the $\tilde{X} \,^2 \Sigma^+$ and $\tilde{A} \,^2 \Pi_{1/2}$ states. The basis set included J = 1/2 through 7/2 whereas the maximum *J*-value associated with the Stark spectra is 3/2. This finite truncation of the infinite matrices was adequate to assure that the introduced error was less than the estimated measurement



FIG. 2. The laser excitation spectrum in the region of the $1_1^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band of YbOH. The assignment and stick spectrum associated with the ¹⁷⁴YbOH isotopologue were obtained using a rotation temperature of 20 K and the optimized parameters.

uncertainty (~10 MHz). The measured Stark shifts of Table V were input to a nonlinear least squares fitting program to determine the optimized values for the magnitude of the molecular frame electric dipole moments, $|\vec{\mu}_{el}|$, and associated errors which are given in Table VI.

effective Hamiltonian [16]:

$$\hat{H}^{Zee} = g_L \mu_B \hat{L}_z \hat{B}_z + g_S \mu_B \hat{S}_z \hat{B}_z + g_I \mu_B (\hat{S}_x \hat{B}_x + \hat{S}_y \hat{B}_y) + g'_I \mu_B (e^{-2i\phi} \hat{S}_+ \hat{B}_+ + e^{+2i\phi} \hat{S}_- \hat{B}_-),$$
(2)

The Zeeman effect for the ${}^{O}P_{12}$ branch features of the $0_{0}^{0}\tilde{A} {}^{2}\Pi_{1/2} - \tilde{X} {}^{2}\Sigma^{+}$ band system was modeled using the

where $\hat{\mu}_B$ is the Bohr magneton; $\hat{S}_{x,y}$ and $\hat{B}_{x,y}$ refer to the *x*, *y*-molecule-fixed components of the electronic spin angular

TABLE III. Observed and calculated line positions in wave number (cm⁻¹) of the $1_1^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+ A^2\Pi_{1/2}$ band system of 174 YbOH.

	N''	J'	Observed	Obs-Calc		N''	J^{\prime}	Observed	Obs-Calc
$\overline{^{O}P_{12}}$	2	1/2	16792.8254	-0.0016	${}^{Q}Q_{11}$	1	3/2	16794.3491	0.0000
	3	3/2	16791.9023	-0.0008		2	5/2	16794.4235	0.0012
	4	5/2	16790.9987	0.0008		3	7/2	16794.5146	0.0005
	5	7/2	16790.1119	0.0005		4	9/2	16794.6241	-0.0004
${}^{P}P_{11}$	1	1/2	16794.2485	0.0013		5	11/2	16794.7522	-0.0015
	2	3/2	16794.2529	0.0005		6	13/2	16794.9012	-0.0004
	3	5/2	16794.2770	0.0008		7	15/2	16795.0686	0.0005
	4	7/2	16794.3195	0.0009		8	17/2	16795.2552	0.0019
	5	9/2	16794.3797	0.0001	${}^{Q}R_{12}$	1	5/2	16794.3440	0.0004
	6	11/2	16794.4591	-0.0001		2	7/2	16794.4137	0.0007
	7	13/2	16794.5580	0.0006		3	9/2	16794.5010	-0.0001
	8	15/2	16794.6717	-0.0025		4	11/2	16794.6071	-0.0008
${}^{P}Q_{12}$	1	1/2	16794.2425	0.0008		5	13/2	16794.7321	-0.0013
	2	3/2	16794.2435	0.0004		6	15/2	16794.8772	-0.0004
	3	5/2	16794.2638	0.0006		7	17/2	16795.0418	0.0014
	4	7/2	16794.3001	-0.0019		8	19/2	16795.2209	-0.0011
	5	9/2	16794.3597	0.0004	${}^{R}R_{11}$	0	3/2	16795.7098	-0.0009
	6	11/2	16794.4357	0.0005		1	5/2	16796.7083	-0.0009
	7	13/2	16794.5303	0.0006		2	7/2	16797.7253	-0.0010
	8	15/2	16794.6434	0.0006		3	9/2	16798.7620	0.0000



FIG. 3. The observed laser excitation spectrum in the region of the $1_0^1 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ band head of YbOH. The assignment and stick spectrum associated with the ${}^{1/4}$ YbOH isotopologue were obtained using a rotation temperature of 20 K and the optimized parameters. The unusual ordering of the branches is caused by the unusually large Λ doubling in the $\tilde{A} \, {}^2\Pi_{1/2}(1, 0, 0)$ state.

momentum and magnetic field, respectively; and ϕ is the azimuthal angle of the electronic coordinates. $\hat{S}_{+,-}$ and $\hat{B}_{+,-}$ refer to the raising and lowering operators expressed in the molecule-fixed axis. The small magnetic moments associated with end-over-end rotation and the proton nuclear spin have been ignored. Only the middle two terms of Eq. (2) are required for modeling the $\tilde{X}^2 \Sigma^+(0,0,0)$ state. In the effective Hamiltonian approach used here all g factors are considered variables and in principle six parameters [four for $\tilde{A}^{2}\Pi_{1/2}(0,0,0)$ and two for $\tilde{X}^{2}\Sigma^{+}(0,0,0)$] are required to model the Zeeman spectrum of the $0_0^0 \tilde{A} \ ^2\Pi_{1/2} - \tilde{X} \ ^2\Sigma^+$ band. Based upon the analysis of the Zeeman spectrum of the $(0, 0)A^2\Pi_{1/2} - X^2\Sigma^+$ band of YbF [17], it is expected that g_L and g_S for the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ and $\tilde{X}^{2}\Sigma^{+}(0,0,0)$ states of YbOH will be very near to 1.00 and 2.002 and that g_l and g'_l will be approximately given by the Curl-type relations: $g_l \approx -\gamma/2B$ and $g'_l \approx p/2B$. Making the reasonable assumption that the Λ -doubling parameter $p + 2q \approx p$, the derived field-free parameters of Table VI give $g_l[\tilde{X}\ ^2\Sigma^+(0,0,0)] = 5.5 \times 10^{-3} \text{ and } g'_l[\tilde{A}\ ^2\Pi_{1/2}(0,0,0)] =$ -0.865. An estimate for $g_l[\tilde{A}^2 \Pi_{1/2}(0,0,0)]$ is more difficult because the spin-rotation parameter, γ , for the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ state is indeterminable. Based upon the YbF results [17], it is expected that $g_l[\tilde{A} \ ^2\Pi_{1/2}(0,0,0)] \approx 0$. The Zeeman spectrum of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band was modeled by constraining the required six g factors to these values: $\tilde{A}^2 \Pi_{1/2}$; $g_S = 2.002$, $g_L = 1.000$, $g'_l = -0.865$, $g_l = 0$, and $\tilde{X}^2 \Sigma^+$; $g_S = 2.002$, $g_l = 5.5 \times 10^{-3}$.

Simulating the optical spectra was particularly crucial for making the rotational branch assignments. To that end, the electric dipole transition moment matrices for the ${}^{2}\Sigma^{+}$ - ${}^{2}\Pi$ transition were constructed in a Hund's case (a) basis. The 4×2 transition moment was obtained by cross multiplication of the transition moment matrix by the Hund's case (a) eigenvectors of the $\tilde{A}^2 \Pi_{1/2}(\nu_1, 0, 0)$ and $\tilde{X}^2 \Sigma^+(\nu_1, 0, 0)$ states. The transition moment was squared, multiplied by a Boltzmann factor commensurate with a rotational temperature and used in conjunction with a Lorentzian line shape to predict each spectral feature. Simulations of the optical Stark and Zeeman spectra were obtained in a similar fashion. In these cases, 16×8 transition moment matrices were constructed in a Hund's case (a) basis set for the $\tilde{X}^2 \Sigma^+$ and $\tilde{A}^2 \Pi_{1/2}$ for J = 1/2 through 7/2 and cross multiplied by the Hund's case (a) eigenvectors of the $\tilde{A}^2 \Pi_{1/2}(\nu_1, 0, 0)$ and $\tilde{X}^2 \Sigma^+(\nu_1, 0, 0)$ states.

V. DISCUSSION

It has been demonstrated that intense beams of an internally cold sample of YbOH can be generated via an ablationreaction scheme. The precisely measured transition wave numbers for the $0_0^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$, $1_1^0 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$,

Lines	N''	J'	Observed	Obs-Calc	Lines	N''	J'	Observed	Obs-Calc
$\overline{^{O}P_{12}}$	2	1/2	17906.3830	0.0007	${}^{R}R_{11}$	2	7/2	17911.5217	-0.0012
	3	3/2	17905.4024	0.0000		3	9/2	17912.5999	0.0004
	4	5/2	17904.4382	-0.0001		4	11/2	17913.6912	-0.0012
	5	7/2	17903.4897	-0.0005		5	13/2	17914.8019	0.0003
	6	9/2	17902.5568	-0.0011	$^{\mathcal{Q}}Q_{11}$	0	1/2	17907.8571	-0.0001
${}^{P}Q_{12}$	1	1/2	17907.8990	0.0003		1	3/2	17907.8603	0.0001
	2	3/2	17907.9442	0.0006		2	5/2	17907.8793	0.0000
	3	5/2	17908.0046	0.0000		3	7/2	17907.9132	-0.0010
	4	7/2	17908.0810	-0.0009		4	9/2	17907.9648	-0.0002
	5	9/2	17908.1752	-0.0002		5	11/2	17908.0321	0.0006
	6	11/2	17908.2853	0.0000		6	13/2	17908.1130	-0.0008
	7	13/2	17908.4137	0.0022		7	15/2	17908.2113	-0.0004
	8	15/3	17908.5533	-0.0010		8	17/2	17908.3256	0.0004
	9	17/3	17908.7132	-0.0003		9	19/2	17908.4542	-0.0001
	10	19/3	17908.8897	0.0003		10	21/2	17908.5992	0.0003
	11	21/3	17909.0810	-0.0009		11	23/2	17908.7604	0.0013
	12	23/3	17909.2912	0.0000		12	25/2	17908.9357	0.0011
${}^{P}P_{11}$	1	1/2	17907.9028	0.0001		13	27/2	17909.1231	-0.0025
	2	3/2	17907.9508	0.0005		14	29/2	17909.3319	-0.0001
	3	5/2	17908.0145	0.0004		15	31/2	17909.5545	0.0008
	4	7/2	17908.0937	-0.0003	${}^{Q}R_{12}$	1	3/2	17907.8571	0.0009
	5	9/2	17908.1901	-0.0001		2	5/2	17907.8725	-0.0001
	6	11/2	17908.3042	0.0014		3	7/2	17907.9036	-0.0012
	7	13/2	17908.4335	0.0018		4	9/2	17907.9535	0.0006
	8	15/3	17908.5762	-0.0009		5	11/2	17908.0175	0.0008
	9	17/3	17908.7388	-0.0002		6	13/2	17908.0953	-0.0010
	10	19/3	17908.9165	-0.0010		7	15/2	17908.1908	-0.0007
	11	21/3	17909.1120	-0.0007		8	17/2	17908.3035	0.0011
	12	23/3	17909.3242	-0.0004		9	19/2	17908.4278	-0.0010
	13	25/3	17909.5545	0.0011		10	21/2	17908.5719	0.0011
	14	27/3	17909.7992	0.0002		11	23/2	17908.7297	0.0015
						12	25/2	17908.9024	0.0012
						13	27/2	17909.0869	-0.0026
		rm	$s = 0.00091 cm^{-1}$			14	29/2	17909.2931	-0.0002

TABLE IV. Observed and calculated line positions in wave number (cm⁻¹) of the $1_0^1 \tilde{A} \, {}^2\Pi_{1/2} - \tilde{X} \, {}^2\Sigma^+$ band system of 174 YbOH.

and $1_0^1 \tilde{A}^2 \Pi_{1/2} - \tilde{X}^2 \Sigma^+$ bands will facilitate the development of optical laser cooling schemes. Furthermore, this information will be critical for implementing YbOH-based EDM measurements. Precise predictions of other transitions for these three bands can be readily derived using the spectroscopic parameters given in Table VI.

The determined fine structure parameters also provide information about electronic states not directly probed. As is the case for YbF [18], γ for $\tilde{X} \,^2\Sigma^+$ depends strongly on the vibrational state (see Table VI) [i.e., $\tilde{X} \,^2\Sigma^+(0,0,0)$: -0.002 707(19) cm⁻¹ and $\tilde{X} \,^2\Sigma^+(1,0,0)$: -0.00369(7) cm⁻¹]. The spin-rotation interaction in the $\tilde{X} \,^2\Sigma^+$ state is dominated by the second-order contribution [16],

$$\gamma^{(2)} = 2\sum_{2\Pi} \frac{\langle {}^{2}\Sigma_{-1/2} | BL^{-} | {}^{2}\Pi_{1/2} \rangle \langle {}^{2}\Pi_{1/2} | \sum_{i} a_{i} l_{i}^{+} s_{i}^{-} | {}^{2}\Sigma_{1/2} \rangle}{T({}^{2}\Pi) - T({}^{2}\Sigma)},$$
(3)

where the microscopic form of the spin-orbit operator has been used and the summation runs over all ${}^{2}\Pi_{1/2}$ states.

The primary configuration for the $\tilde{X} {}^{2}\Sigma^{+}$ state has a single unpaired electron in a Yb⁺-centered 6s / 6p hybrid orbital:

$$\tilde{X}^{2}\Sigma^{+}:([\text{Xe}]4f^{14})_{\text{Yb}^{+}}\pi^{4}_{\text{OH}^{-}(1\pi)}\sigma^{1}_{\text{Yb}^{+}(6s6p_{0})}.$$
 (4)

It is likely that the dominant configuration for the $\tilde{A}^2 \Pi_{1/2}$ state has a sole unpaired electron in a Yb⁺-centered $6p_{\pm 1}/5d_{\pm 1}$ hybrid orbital:

$$\tilde{A}^{2}\Pi_{1/2}:([Xe]4f^{14})_{Yb^{+}}\pi^{4}_{OH^{-}(1\pi)}\pi^{1}_{Yb^{+}(6p_{\pm 1}5d_{\pm 1})}.$$
 (5)

The potential energy surface for the $\tilde{A}^2 \Pi_{1/2}$ state is very similar to that of the $\tilde{X}^2 \Sigma^+$ state and the interaction between these two states alone would not explain the strong vibrational dependence of γ because of the near diagonal nature of the Franck-Condon factors. Other possible low-lying states of ${}^2\Pi$ symmetry arise from the promotion of the filled Yb⁺-centered 4*f* orbital of the $\tilde{X}^2 \Sigma^+$ state configuration to the $\sigma^1_{Yb^+(6s6p_0)}$ orbital:

$$([Xe]4f^{13})_{Yb^{+}}\pi^{4}_{OH^{-}(1\pi)}\sigma^{2}_{Yb^{+}(6s6p_{0})}$$

$$\rightarrow {}^{2}\Pi_{i}, {}^{2}\Phi_{i}, {}^{2}\Delta_{i}, \text{and} {}^{2}\Sigma^{+}.$$
(6)



FIG. 4. Left: The field-free and Stark spectra for the ${}^{R}R_{11}(0)$ line with parallel polarization ($\Delta M_J = 0$) and a field strength of 3038 V/cm. Right: The associated energy levels for the 174 YbOH isotopologue as a function of electric field strength and assignment.

The potential energy surface for states arising from this configuration will be significantly different from that for the $\tilde{A} \,^2 \Pi_{1/2}$ and $\tilde{X} \,^2 \Sigma^+$ states. The combined interaction between the $\tilde{X} \,^2 \Sigma^+$ state with the $\tilde{A} \,^2 \Pi_{1/2}$ state and the $\,^2 \Pi_{1/2}$ state arising from Eq. (6) can explain the strong vibrational dependence for the $\gamma \, (\tilde{X} \,^2 \Sigma^+)$ state.

A large change in the Λ -doubling parameter, p + 2q, is also observed upon vibrational excitation of the Yb-OH stretching mode of the $\tilde{A}^2 \Pi_{1/2}$ state [i.e., from -0.438 07(7) cm⁻¹ to -0.5345(1) cm⁻¹]. It is reasonable to assume that $p + 2q \approx p$ and that this parameter is dominated by second-order contributions [16] analogous to Eq. (3). The strong vibrational dependence is indicative of an interaction of at least two states

TABLE V. Observed and calculated Stark shift (MHz) in parallel polarization of the $0_0^0 \tilde{A} \ ^2\Pi_{1/2} - \tilde{X} \ ^2\Sigma^+$ band system of ¹⁷⁴YbOH.

Lines	$M_{J'}$	$M_{J'}$	Field (V/cm)	Shift (MHz)	Obs-calc (MHz)
$\overline{{}^{O}P_{12}(2)}$	-1	-1	5104	-87	-3
	-1	-1	4613	-65	3
	-1	-1	3038	-38	-9
${}^{R}R_{11}(0)$	0	0	3575	289	15
	0	0	3038	197	-2
	0	0	1519	32	-18
${}^{Q}Q_{11}(0)$	0	0	1519	55	8
	0	0	506	18	13
			Std. fit: 11	MHz	

of ${}^{2}\Sigma$ symmetry. One of these states most likely has the dominant configuration given in Eq. (6) while, by analogy to BaOH [19], the other state should be from the configuration:

$${}^{2}\Sigma^{+}:([Xe]4f^{14})_{Yb^{+}}\pi^{4}_{OH^{-}(1\pi)}\sigma^{1}_{Yb^{+}(6p_{0}5d_{0})}.$$
(7)

The pure precession and unique perturber approximation [20], which gives the relationship $p \approx \frac{4AB}{\Delta E_{\Pi\Sigma}}$, can be used to estimate the energy of the perturbing ${}^{2}\Sigma^{+}$ state of Eq. (7), assuming that this state and the $\tilde{A}^2 \Pi_{1/2}$ state form a *p* complex (i.e., σ [Yb⁺(6p₀5d₀)] \approx 6p₀(Yb⁺) and π [Yb⁺(6p_{±1}5d_{±1})] \approx $6p_{\pm 1}(Yb^+)$). The experimentally determined $p + 2q \approx$ $p \approx -0.438$ when combined with the spin-orbit A, and rotation, *B*, parameters of 1350 and 0.25305 cm^{-1} gives $E[{}^{2}\Sigma^{+}(\pi^{4}_{\mathrm{OH}^{-}(1\pi)}\sigma^{1}_{\mathrm{Yb}^{+}(6p_{0}5d_{0})})] \approx 20440 \,\mathrm{cm}^{-1}$. It is noteworthy that the $B^2\Sigma^+$ state of CaF is analogous to the $^2\Sigma^+$ state of Eq. (7). The production of an ultracold sample of CaF via magneto-optical trapping [21,22] uses the $(0,0)B^2\Sigma^+$ – $X^{2}\Sigma^{+}$ transition as the primary slowing transition because of a favorable branching ratio. The energy estimate for $^{2}\Sigma^{+}(\pi^{4}_{OH^{-}(1\pi)}\sigma^{1}_{Yb^{+}(6p_{0}5d_{0})})$ provided here may assist in future attempts to identify a similar state and transition for YbOH.

The experiment only determines the magnitude of the molecular frame electric dipole moments, $|\vec{\mu}_{el}|$, but it is realistic that the charge distribution is $Yb^{\delta+}(OH)^{\delta-}$ for the $\tilde{X} \,^2\Sigma^+(0,0,0)$ state. The charge distribution for the $\tilde{A} \,^2\Pi_{1/2}(0,0,0)$ may be reversed (i.e., $Yb^{\delta-}(OH)^{\delta+}$) because the unpaired Yb⁺-centered electron is more easily polarized away from the Yb-OH bond. The determined ground state



FIG. 5. Left: The field-free and optical Zeeman spectra in the vicinity of the ${}^{O}P_{12}(3)$ line recorded at a field of 64 G with parallel polarization $(\Delta M_J = 0)$. The predicted spectrum for the 174 YbOH isotopologues was obtained using a narrower linewidth than that of the observed spectrum (10 MHz vs 30 MHz) to highlight the underlying splitting. Right: The energy level tuning for the 174 YbOH isotopologue as function of magnetic field strength along with the assignment. The effecting g_J -factor for the ground and excited state levels of the induced ${}^{O}O_{11}(3)$ line are of the same magnitude and sign resulting in a sharp spectral feature whereas those for the ${}^{O}O_{11}(3)$ line are of the same magnitude but opposite sign resulting in a broad, partially resolved, spectral feature. The spacing between the ${}^{O}O_{11}(3)$ induced transition and ${}^{O}P_{12}(3)$ line provides a direct measure of the ρ doubling in the $\tilde{X} \, {}^{2}\Sigma^{+}(0, 0, 0)$ state.

	Parameter	¹⁷⁴ YbOH (0,0,0)	¹⁷² YbOH (0,0,0)	¹⁷⁴ YbOH (1,0,0)
$\overline{ ilde{X}^{2}\Sigma^{+}}$	<i>B</i> ″	0.245116257ª	0.245387(6)	0.243681(8)
	$10^7 D''$	2.029 ^a	2.359 ^b	2.168 ^b
	γ"	-0.002707ª	-0.00270(2)	-0.00369(7)
	$10^7 \gamma_D'$	1.59 ^a		
	T_0			529.3269(3)
	$ \vec{\mu}_{el} $ (D)	1.9(2)		
	g_l	0.0055°		
$\tilde{A}^2 \Pi_{1/2}$	A'	1350 (fixed)	1350 (fixed)	1350 (fixed)
	B'	0.253052(3)	0.253329(6)	0.253198(3)
	$10^{7}D'$	2.319 ^b	2.506 ^b	2.478 ^d
	p + 2q'	-0.43807(7)	-0.43850(4)	-0.5346(1)
	$10^{6}(p+2q)_{D'}$	3.8(8)	3.4(4)	-17.3(7)
	T_0	17998.5875(2)	17998.61549(9)	18582.8708(3)
	$ \vec{\mu}_{el} $ (D)	0.43(10)		
	g'_l	-0.865°		

TABLE VI. Spectroscopic parameters (cm⁻¹) for the $\tilde{X} \,^2\Sigma^+$ and $\tilde{A} \,^2\Pi_{1/2}$ states of ¹⁷⁴YbOH and ¹⁷²YbOH.

^aFixed to PPMODR values (Ref. [11]).

^bFixed to values from analysis of high temperature sample (Ref. [10]).

^cObtained from Curl-type relationship. g_L and g_S constrained to 1.000 and 2.002.

^dFixed to value extrapolated from the that used for 174 YbOH(0, 0, 0).

value of 1.9(2) D is significantly larger than the recently predicted 1.1 D value obtained using relativistic coupled cluster theory [23]. That calculation predicted a Yb^{δ +}(OH)^{δ -} charge distribution. Excited state $\vec{\mu}_{el}$ values were not predicted. The determined value of 1.9(2) D is also significantly smaller than the assumed 4 D value used for modeling the polarization of the $\tilde{X}^{2}\Sigma^{+}(0, 1^{1}, 0)$ state relevant to the EDM measurement [1]. The 1.9(2) D and 0.43(10) D values for the $\tilde{X}^{2}\Sigma^{+}(0,0,0)$ and $\tilde{A}^{2}\Pi_{1/2}(0,0,0)$ states are also significantly smaller than the 3.91(4) D (Ref. [24]) and 2.46(3) D (Ref. [25]) values for the $X^{2}\Sigma^{+}(v=0)$ and $A^{2}\Pi_{1/2}(v=0)$ states of YbF. For both YbF and YbOH the $\vec{\mu}_{el}$ values are much less than the ~ 10 D value expected for a Yb⁺¹F⁻¹ and $Yb^{+1}(OH)^{-1}$ charge distribution. The reduction from the $Yb^{+1}F^{-1}$ or $Yb^{+1}(OH)^{-1}$ value is primarily due to the large induced dipole moment caused by the highly polarizable Ybcentered unpaired electron, but also has a major contribution from the induced dipole moment on the closed shell F- and OH⁻ ligands The dipole moment of the OH⁻ ligand, which has a $O^{\delta-}H^{\delta+}$ charge distribution, opposes that of the Yb-OH bond causing $\vec{\mu}_{el}$ YbOH to be less than that for YbF.

The simple electrostatic model developed for CaOH [26], which is a modified version of that developed by Törring *et al.* [27] for diatomic molecules, is useful for estimating ground state $\vec{\mu}_{el}$ values for both YbOH and YbF. Mestdagh and Visticot [28] developed a slightly more sophisticated electrostatic model for the alkali and alkaline earth monohydroxides, but the simpler model used here is adequate. In these models, $\vec{\mu}_{el}$ is assumed to be the sum of the dipole moment produced by the Yb⁺¹ – X⁻¹ ion pair separated by a bond distance, R_{Yb-X} , a cation moment, $\vec{\mu}_{el}^+$, and anion centered moment, $\vec{\mu}_{el}^-$:

$$\vec{\mu}_{el} = eR_{Yb-X} - \mu_{el}^+(Yb^+) - \mu_{el}^-(X^-).$$
(8)

The cation centered moment, $\vec{\mu}_{el}^+$, is a result of anion-induced polarization of the Yb⁺¹ center, which is treated as an unpolarizable Yb⁺² core and a highly polarizable unpaired electron displaced from the Yb-X bond by a distance Δr ,

$$\mu_{el}^{+}(Yb^{+}) = e\Delta r$$

= $\alpha^{+} \left\{ \frac{e}{(R_{Yb-X} + \Delta r)^{2}} + \frac{2\mu_{el}^{-}(X^{-})}{(R_{Yb-X} + \Delta r)^{3}} \right\},$ (9)

where α^+ is an effective dipole polarizability of Yb⁺. The first term in brackets in Eq. (9) is the X^- point charge induced contribution and the second is that induced by the anion dipole. In the case of diatomic YbX, the anion centered moment, $\vec{\mu}_{el}(X^-)$, is a result of induced polarization of the closed shell X^{-1} center caused by both the Yb⁺² core and the unpaired electron. In the case of triatomic YbX, there are three contributions to $\vec{\mu}_{el}(X^-)$: those resulting from induced polarization of (OH)⁻¹ by the Yb⁺² core and the unpaired electron, and that from the dipole moment of a free (OH)⁻¹ anion, $\mu_{el}^{\text{free}}(X^-)$:

$$\mu_{el}^{-}(X^{-}) = \alpha^{-} \left\{ \frac{2e}{R_{Yb-X}^{2}} - \frac{e}{(R_{Yb-X} + \Delta r)^{2}} \right\} + \mu_{el}^{\text{free}}(X^{-}),$$
(10)

where α^{-} is an effective dipole polarizability of the anion. Substitution of Eq. (9) into (10) gives the expression for the displacement of the unpaired, Yb-centered electron, Δr :

$$\Delta r = \frac{\alpha^{+}}{(R_{Yb-X} + \Delta r)^{2}} + \frac{4\alpha^{+}\alpha^{-}}{R_{Yb-X}^{2}(R_{Yb-X} + \Delta r)^{3}} - \frac{2\alpha^{+}\alpha^{-}}{(R_{Yb-X} + \Delta r)^{5}} + \frac{2\alpha^{+}\mu_{el}^{\text{free}}(X^{-})}{(R_{Yb-X} + \Delta r)^{3}e}.$$
 (11)

With the possible exceptions of α^+ and α^- , estimates for the parameters required for implementation of Eqs. (8)–(11)to predict ground state $\vec{\mu}_{el}$ values for YbOH and YbF are readily obtained. An R_{Yb-F} bond distance of 2.0196 Å for the $X^{2}\Sigma^{+}(v=0)$ state of YbF is obtained from the experimental B_0 value [29] of 7233.2871 MHz. An $R_{\rm Yb-OH}$ bond distance of 2.037 Å for the \tilde{X} ² $\Sigma^+(0, 0, 0)$ state of YbOH is obtained using the ground state B_0 value of 7348.4005 MHz derived from the analysis of the microwave spectrum [11] and the predicted ground state [30] OH⁻ bond distance of 1.823 Å. The *ab initio* predicted [30] $\vec{\mu}_{el}$ for OH⁻ of 1.10 D, which as mentioned has a $O^{\delta-}H^{\delta+}$ charge distribution and opposes that of the Yb-OH bond dipole, is a reasonable estimate $\mu_{a}^{\text{free}}(\text{OH}^-)$. The effective polarizabilities α^- and α^+ are more difficult to estimate. The static dipole polarizability of free ground state Yb⁺ is calculated [31] to be 9.19 Å^3 , while those for ground state OH- and F- are calculated [32] to be 3.97 and 2.61 \AA^3 , respectively. The effective dipole polarizabilities α^- and α^+ needed to model YbOH and YbF are reduced from these free ion values due to overlapping charge distributions. The anions also undergo an additional reduction due to Pauli repulsion [26]. The effective polarizabilities α^- for OH⁻ and F⁻ derived from modeling experimental measured $\vec{\mu}_{el}$ values and dissociation energies [27,28] are of 1.2 and 0.69 \AA^3 , respectively, and will be assumed here. The calculated [33] dipole polarizability α^+ for the ground state of free Ba^+ is 18.2 Å³, whereas the effective polarizabilities used in modeling the experimental $\vec{\mu}_{el}$ values and dissociation energies for BaF and BaOH [27,28] were 12.0 \AA^3 . Assuming a similar 34% reduction from the free ion value gives an effective α^+ of 6.05 Å³ for ground state Yb⁺. Using these values $[R_{Yb-OH} = 2.037 \text{ Å}, R_{Yb-F} = 2.0196 \text{ Å}, \mu_{el}^{\text{free}}(\text{OH}^-) = 1.10 \text{ D}, \alpha^+(\text{Yb}^+) = 6.05 \text{ Å}^3, \alpha^-(\text{OH}^-) =$ 1.2 Å³, and $\alpha^{-}(F^{-}) = 0.69$ Å³] predicts $\vec{\mu}_{el}$ values of 4.34 and 1.89 D for the ground states of YbF and YbOH, which are in good agreement with the experimental values of 3.91(4) D (Ref. [24]) and 1.9(2) D (present work). The predicted shift of the unpaired electron, Δr , for YbF and YbOH are 0.859 and 0.969 Å, respectively. The 3.91(4) D (Ref. [24]) value for the $X^{2}\Sigma^{+}(v=0)$ state of YbF can be reproduced if $\alpha^+(Yb^+) = 7.08 \text{ Å}^3$, which then gives $\vec{\mu}_{el}$ for $\tilde{X} \,^2 \Sigma^+(0, 0, 0)$ of 1.40 D, which is also in fair agreement with the observed value of 1.9(2) D.

Although the Zeeman effect was primarily used as a means of determining the spin-rotation splitting, γ , for the $\tilde{X} \,^2\Sigma^+(0, 0, 0)$ state, it also provides insight into the nature of the excited electronic state. It has been assumed that the energy levels of the observed excited electronic states are the $\nu_1 = 0$ and 1 vibrational levels of the $\tilde{A} \,^2\Pi_{1/2}$ electronic state. This assumed nature is based primarily from analogy with

YbF. As pointed out long ago [34] there is an isomorphism between field-free energy level patterns of the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Sigma^{\pm}$ states. The field-free excited rotational energy level pattern observed for what has been assumed to be the $\tilde{A} {}^{2}\Pi_{1/2}(0, 0, 0)$ state could be equally well modeled as a $\tilde{A} {}^{2}\Sigma^{-}(0, 0, 0)$ state having *B* and γ of 0.253 02 and 0.068 08 cm⁻¹, respectively. This energy level pattern is that of a typical Hund's case (b) ${}^{2}\Sigma^{\pm}$ state where the rotational spacing is significantly larger than the spin-rotation splitting (ρ doubling). A state of ${}^{2}\Sigma^{-}$ symmetry could arise from a $\cdots \pi^{2}\sigma^{1}$ configuration. The observed Zeeman effect can be used to unambiguously determine between these two electronic state designations.

In the Hund's case (b) limit, the Zeeman-induced shift in energy is given by

$$\Delta E^{Zee} = g_J \mu_B B_z M_J; \quad g_J \equiv g_S \frac{[S(S+1) + J(J+1) - N(N+1)]}{2J(J+1)}.$$
(12)

For the ${}^{O}P_{12}(3)$ line presented in Fig. 5 the upper energy level in a $\tilde{A} {}^{2}\Sigma^{-}(0, 0, 0)$ state designation corresponds to S = 1/2, N = 1, and J = 3/2. The $\tilde{A} {}^{2}\Sigma^{-}(0, 0, 0)$ model [Eq. (12)] predicts that $g_{J} = g_{S}/3 \approx 2/3$, whereas the observed value for this energy level is approximately 0.26. If the $\tilde{A} {}^{2}\Pi_{1/2}(0, 0, 0)$ model is used then the magnetic tuning comes primarily from the parity-dependent term, g'_{I} , of Eq (2), because the magnetic moments from electronic spin \vec{S} and electronic orbital angular \vec{L} momenta nearly cancel. The large spin-orbit parameter A, relative to the rotational parameter B, results in an energy level pattern that is of a molecule near the Hund's case (a) limit. The diagonal in J, Hund's case (a) matrix elements for the g'_{I} term are [16]

$$\langle \Lambda; S, \Sigma; J, \Omega, M_J | g'_I \mu_B (e^{-2i\phi} \hat{S}_+ \hat{B}_+ + e^{+2i\phi} \hat{S}_- \hat{B}_-) | \Lambda'; S, \Sigma'; J, \Omega', M_J \rangle$$

$$= -\mu_B B_z g'_I \sum_{q=\pm 1} \delta_{\Lambda,\Lambda\mp 1} (-1)^{+S-\Sigma-\Omega-M_J} (2J+1) \begin{pmatrix} J & 1 & J \\ -M_J & 0 & M_J \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} [S(S+1)(2S+1)]^{1/2} \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega' \end{pmatrix}.$$

$$(13)$$

The quantum numbers associated with the basis set for the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ state are S = 1/2, $\Lambda = +1$, $\Sigma = -1/2$, $\Omega = +1/2\Lambda' = -1$, $\Sigma' = +1/2$, and $\Omega' = -1/2$, which upon substitution into Eq. (13) and then conversion to a parity basis, give:

$$\langle \Lambda; S, \Sigma; J, \Omega, M_J, \pm | H^{Zee}(\text{parity}) | \Lambda'; S, \Sigma'; J, \Omega', M_J, \pm \rangle$$

$$= g_J \mu_B B_z M_J; \quad g_J \equiv \pm g'_I \frac{(J+1/2)}{2J(J+1)}.$$
 (14)

The "+/–" values in the expression for g_J are the associated "e/f" parity levels. The *e*-parity levels have $(-1)^{J-1/2}$ parity while the *f*-parity levels have $(-1)^{J+1/2}$ parity. For the ${}^{O}P_{12}(3)$ line presented in Fig. 5 the upper energy level in a $\tilde{A} \,{}^2\Pi_{1/2}(0, 0, 0)$ state designation corresponds to J = 3/2, *f*-parity, and the model predicts that $g_J = -g'_I \times (4/15) = 0.231$, where the g'_I from the Curl-type relationship (-0.865) has been used. The excellent agreement of the observed magnetic tuning $[g_J \text{ (obs.)} \approx 0.26]$ with that obtained assuming an $\tilde{A} \,{}^2\Pi_{1/2}(0, 0, 0)$ state designation $(g_J \text{ [Hund's case (a)]} \approx 0.231)$ vs that poor agreement with the $\tilde{A} \,{}^2\Sigma^-(0, 0, 0)$ state designation $(g_J \text{ [Hund's case (b)]} \approx 2/3)$ is strong experimental evidence that the excited state is the $\tilde{A} \,{}^2\Pi_{1/2}(0, 0, 0)$ analogs to the $A \,{}^2\Pi_{1/2}(v = 0)$ electronic state of YbF.

Tarbutt has shown [35] that the force associated with magneto-optical trapping using the $A^2 \Pi_{1/2} - X^2 \Sigma^+$ transition is primarily determined by the excited state magnetic moment. The unusually large magnetic moment for the $\tilde{A}^2 \Pi_{1/2}$ state of YbOH and the $A^2 \Pi_{1/2}$ state of YbF, which are due to the mixing with other nearby electronic states, will facilitate magneto-optical trapping. The g'_l , and hence the magnetic moment, for the $\tilde{A}^2 \Pi_{1/2}(0, 0, 0)$ state of YbOH (-0.865) is somewhat larger than that for the $A^2 \Pi_{1/2}(v = 0)$ state of YbF (-0.823), suggesting that magneto-optical trapping of

YbOH may prove easier than magneto-optical trapping of YbF.

VI. SUMMARY

The low-*J* branch features for ¹⁷⁴YbOH have been precisely measured and modeled and will facilitate laser cooling and EDM measurements now being undertaken. The magnitude of the molecular frame electric dipole moments, $|\vec{\mu}_{el}|$, for the $\tilde{A} \, {}^2\Pi_{1/2}(0, 0, 0)$ and $\tilde{X} \, {}^2\Sigma^+(0, 0, 0)$ states of YbOH have been determined. A simple electrostatic polarizability model has been shown to fairly accurately predict the $|\vec{\mu}_{el}|$ using an effective dipole polarizability of Yb+, α^+ , of 6.05 Å³. The determined effective polarizability will be useful for modeling $\vec{\mu}_{el}$ of other Yb-containing molecules. The magnetic tuning confirms that the upper energy terminus of the transitions studied here is consistent with a ${}^2\Pi_{1/2}$ assignment. Expressions for the effective g_J factor for the ${}^2\Pi_{1/2}$ state have been derived and used in conjunction with a Curl-type relation to accurately predict the Zeeman tuning.

High-resolution spectroscopic studies of bands previously assigned [10] to transitions involving the degenerate bending modes are now in progress. These bands are more complex than those described here because of strong vibronic coupling. Analysis of the $0_0^0 \tilde{A} \,^2 \Pi_{1/2} - \tilde{X} \,^2 \Sigma^+$ band of the ¹⁷¹YbOH and ¹⁷³YbOH isotopologues is also in progress.

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