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Precision Zeeman-Stark Spectroscopy of the Metastable a(1)[Σ+3] State of PbO

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Proof of principle for a high sensitvity search for the electric dipole moment of the electron using the metastable $a(1)\left[^3\Sigma^+\right]$ state of PbO

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The metastable $a(1)\left[^3\Sigma^+\right]$ state of PbO has been suggested as a suitable system in which to search for the electric dipole moment (EDM) of the electron. We report here the development of experimental techniques allowing high-sensitivity measurements of Zeeman and Stark effects in this system, similar to those required for an EDM search. We observe Zeeman quantum beats in fluorescence from a vapor cell of PbO, with shot-noise limited extraction of the quantum beat frequencies, high counting rates, and long coherence times. We argue that improvement in sensitivity to the electron EDM by at least two orders of magnitude appears possible using these techniques.

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A permanent electric dipole moment (EDM) of the electron d_e would violate parity and time-reversal symmetries [1]. Many extensions of the standard model predict d_e within 1-3 orders of magnitude of the current limit [2]; thus extending the sensitivity to d_e by a few orders of magnitude may offer the exciting possibility of observing new physics beyond the standard model [3].

There is a dramatic advantage to using heavy polar molecules in such searches [4]. Strong hybridization of the atomic orbitals in such molecules leads to enormous internal electric fields along the internuclear axis $\hat{\mathbf{n}}$. The close spacing of levels of opposite parity allows full polarization of this axis along external fields attainable in the laboratory, enhancing the linear Stark effect produced by d_e two or more orders of magnitude beyond that expected in atoms [5]. Still, this theoretical advantage has yet to translate into a competitive limit on d_e.

In this paper we describe several measurements which constitute a proof of principle for a new type of search for d_e. Our experiment uses the metastable $a(1)\left[^3\Sigma^+\right]$ state of PbO. We have earlier proposed to use this state to extend the current bound $|d_e| \leq 1.6 \times 10^{-27}$ e·cm [2] by 2-4 orders of magnitude [6]. The high sensitivity of the proposed EDM experiment relies on several properties of the $a(1)$ state of PbO, including its large enhancement factor [7, 8], and unique possibilities for the rejection of systematic errors [9]. The key technical advance reported here is the ability to create, manipulate, and measure coherent electron spin superpositions in a high-density PbO vapor cell. This leads to measurements of Zeeman and Stark splittings, like those for an EDM search, with narrow linewidths and at high signal-to-noise S/N. With this ability we measured coherence times and quenching cross sections in the vapor cell; demonstrated sensitive, shot-noise limited extraction of Zeeman quantum beat frequencies; and measured Landé g-factors. Finally, we have demonstrated the ability to apply electric fields sufficiently strong to fully polarize the $a(1)$ state.

A barrier to molecule-based searches for d_e has been achieving sufficient numbers of suitable molecules – count rates of 10^4 Hz limited the sensitivity of a recent molecular beam experiment using YbF [10], which was far from systematic limits. To achieve much higher counting rates we developed a specialized oven to heat a novel vapor cell to temperatures of 700°C, where PbO has substantial vapor density, $n \approx 4 \times 10^{13}$ cm^{-3}. The cell contains about 80 cm^3 of PbO vapor of natural isotopic abundance, and has gold foil electrodes for measurements requiring an electric field. The cell and oven sit in a vacuum chamber surrounded by 3 orthogonal Helmholtz coils.

With this apparatus we can populate and detect fluorescence from the metastable state of interest as follows. We populate the $a(1)(v'=5)$ state of ^{208}PbO by laser excitation from the ground state $X(0)(v''=1)$. A dye laser is pumped by the second harmonic of a Nd:YAG laser at a rep. rate of 100 Hz, and delivers 10-20 mJ/pulse of light at wavelength $\lambda \approx 571$ nm propagating in the $\hat{\mathbf{y}}$ direction to the vapor cell. The pulses are ≈ 8 ns long with a linewidth of 1 GHz, comparable to the Doppler width of the transition. The light traverses the vacuum chamber and oven in a 5 cm diam. lightpipe to the cell, then exits through another lightpipe. Fluorescence from the $a(1)(v'=5) \rightarrow X(0)(v''=0)$ decay at $\lambda \approx 548$nm is captured by a third lightpipe orthogonal to the laser beam. The fluorescence passes through an infrared-blocking filter and two interference filters (550 ± 5 nm bandpass), which block scattered laser light and most blackbody radiation from the ovens, while passing the signal of interest to a photomultiplier tube (PMT).

The EDM search and all measurements discussed here use the levels of the $a(1)$ state with total angular momentum J=1. This Hund's case (c) state can have projections Ω of electronic angular momentum $\mathbf{J}_e$ along or against the internuclear axis, $\Omega = \mathbf{J}_e \cdot \hat{\mathbf{n}} = \pm 1$. Even and odd combinations form nominally degenerate parity eigenstates. The degeneracy is broken by the Coriolis coupling between electronic and rotational angular momentum. This splits each level J into two closely spaced states of opposite parity, e and f, with parity $(-1)^J$ and $(-1)^{J+1}$ respectively [11] and separation $\Delta_\Omega(J) =$

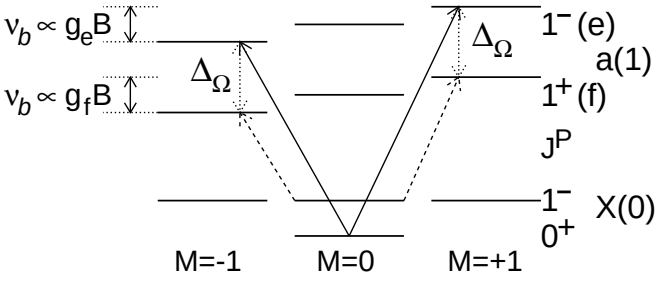

FIG. 1: The energies of the low-lying X(0) and a(1) states in a magnetic field **B** are shown. The coherent $R0$ ($Q1$) transition leading to quantum beats at $\nu_b \propto g_e B$ ($g_f B$) is indicated by solid (dashed) arrows. The Ω-doublet splitting Δ_Ω (which is independent of **B** and M) is shown greatly exaggerated. Transitions between the doublet levels can be driven by an RF electric field at $\nu_{RF} = \Delta_\Omega$ (dotted arrows).

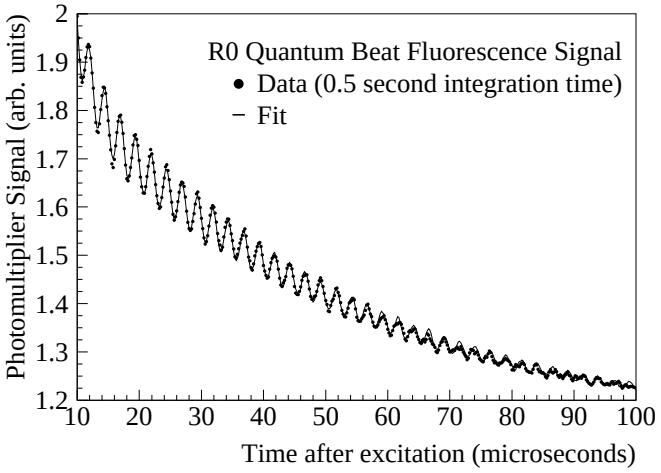

FIG. 2: Zeeman quantum beat data representing 0.5 seconds of integration are shown with a fit to Eq. (1).

$qJ(J+1)$, where $q = 5.6(1)$ MHz for $a(1)(\nu' = 5)$ [12].

In the presence of a static electric field, a non-zero value of d_e results in a linear Stark shift in the $M = \pm 1$ sublevels of these $J = 1$ levels [6, 9]. The current limit on d_e corresponds to a 15-40 mHz shift [7, 8]. To test the method proposed to detect this shift in the EDM search, we studied Zeeman quantum beats in a static magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$ which shifts the $a(1)$ levels by $g_i \mu_B B M/J(J+1)$. Here μ_B is the Bohr magneton, and $g_i = g_e$ (g_f) is the Landé g-factor in the molecule-fixed frame of the e (f) member of the Ω-doublet.

Pulses of $\hat{\mathbf{x}}$-polarized light were used to create a coherent superposition of $M = \pm 1$ sublevels, equivalent to an alignment of the angular momentum **J** along $\hat{\mathbf{x}}$. The B-field removes the $M = \pm 1$ degeneracy so the sublevels evolve at different rates and acquire a phase difference, leading to a precession of the alignment about $\hat{\mathbf{z}}$ [13]. We detect this precession as $\Delta M = 2$ quantum beats which modulate the exponential decay in the unpolarized fluorescence intensity at twice the Larmor frequency, $\nu_b = 2 g_i \mu_B B/hJ(J+1)$. Electric dipole selection rules allow us to selectively excite either parity state of the $J = 1$ Ω-doublet. This is accomplished by tuning the dye laser frequency to either the $X(J = 0^+) \rightarrow a(J = 1^-)$ transition ($R0$ line), or the $X(J = 1^-) \rightarrow a(J = 1^+)$ transition ($Q1$ line), separated by ≈ 18 GHz. The relevant levels and transitions are shown in Fig. 1.

The time-dependent quantum beat fluorescence signals, $I(t)$, were fit to the form (see Fig. 2) :

$$I(t) = \alpha S(t) \times \left[1 + c e^{-t/T_b} \cos(2\pi\nu_b t + \phi)\right] + d + P(t) + \beta L(t). \quad (1)$$

The terms in this equation are as follows. $P(t)$ is an electronic transient associated with switching off the PMT gain during the laser pulse, and $L(t)$ is the residual signal associated with scattered laser light; both are recorded off-line. $S(t)$ describes the fluorescence signal in the absence of quantum beats; this was determined by applying an inhomogeneous magnetic field $dB_z/dz \approx 0.2$ G/cm which caused rapid decoherence of the beats. $S(t)$ is approximately exponential in form, with deviations due to wall quenching and time-dependent acceptance changes resulting from diffusion of the excited molecules. The remaining seven parameters are adjusted to fit the quantum beat signals: scale factors $\alpha, \beta \approx 1$ for the signal and scattered light, respectively; the beat contrast $c \approx 0.1$; a factor $T_b \approx 100$ μs, accounting for shortening of the beat coherence time by collisions; the quantum beat frequency $\nu_b \approx$ 125−400 kHz (corresponding to $B \approx 50-160$ mG); the beat phase ϕ; and the background level due to blackbody radiation from the oven d; in practice $d \approx S(0)$. The fits start $10 - 15$ μs after the laser pulse to lessen the impact of the transients on the fit.

We used data of this type to optimize the cell conditions for the extraction of Zeeman beat frequencies. Collisions with ground state PbO molecules can quench molecules in the excited state and reduce the effective lifetime T_1 of the $a(1)$ state in the cell, and reduce the quantum beat coherence time T_2. We expect

$$\frac{1}{T_1} \simeq \frac{1}{\tau_a} + \frac{1}{\tau_{\rm cell}} + \sigma_1 n v, \text{ and } \frac{1}{T_2} \simeq \frac{1}{T_1} + \sigma_2 n v \quad (2)$$

where $\tau_a \sim 82(2)$ μs is the natural lifetime [6], $\tau_{\rm cell}$ is an approximate time constant for quenching on the cell walls, σ_1 is the state quenching cross-section, v is the average relative velocity ($v \approx$ 400 m/s) and σ_2 is the cross-section for beat quenching but state preserving collisions ($\sigma_2 n v \simeq 1/T_b$ in Eq. (1)). The optimal S/N in beats is obtained when the density is adjusted so the collisional decoherence rate is comparable to the decay rate of the excited state, $(\sigma_1 + \sigma_2) n v \simeq 1/\tau_a + 1/\tau_{\rm cell}$. We extracted σ_1 and σ_2 by approximating $S(t)$ with $\exp(-t/T_1)$ in the fits to Eq. (1), then observing the changes in T_1 and T_2 as

the number density in the cell was varied by more than an order of magnitude (by changing the cell temperature). We find $\sigma_1 \approx 0.4 \times 10^{-14}$ cm^2 and $\sigma_1 + \sigma_2 \approx 1.8 \times 10^{-14}$ cm^2, with a factor of two uncertainty, reflecting the range of results obtained with different cells and from systematic uncertainties in the fitting. The results imply an optimal cell density $n \approx 3 \times 10^{13}$ cm^{-3} (corresponding to a cell temperature of 690°C), enabling the experiment to run near its originally proposed sensitivity [6].

We ran at this optimal condition to determine the noise in our extraction of Zeeman beat frequencies.We typically achieved a sensitivity $\delta\nu_b \approx 50$ Hz$/\sqrt{\text{Hz}}$ for integration periods $T < 1$s. Drift in the ambient magnetic field between laser shots dominated the uncertainty over longer intervals. This short-term sensitivity matches the shot-noise limited uncertainty in frequency expected from :

$$\delta\nu_b \approx \frac{\kappa\sqrt{2}}{2\pi c T_2 \sqrt{\dot{N}}} \approx \frac{50 \text{ Hz}}{\sqrt{\text{Hz}}} \tag{3}$$

where $\sqrt{2}$ comes from fitting the phase; κ is an excess noise factor depending on the ratio $S(0)/d$; $\dot{N} \gtrsim 1\times10^7/s$ is the average detected fluorescence count rate, and $T_2 \approx 50$ μs. We find $\kappa \approx 3$ through modeling. We note that the measured value of $\dot{N}$ is close to expectations, based on the estimated efficiencies for our current setup. The excitation efficiency is $\varepsilon_e \approx 0.03\%$, based on the available laser power, rep. rate, and estimated $X(0) - a(1)$ excitation cross-section [6, 9]. The detection efficiency is $\varepsilon_d \approx 0.003\%$, based on the PMT quantum efficiency and simulated geometric collection efficiency.

We used this apparatus to make precise measurements of g_e and g_f for the $J = 1$ levels of the $a(1)$ state. These quantities are of interest for two reasons. The deviation of $\bar{g} = (g_e+g_f)/2$ from 2 is a measure of spin-orbit mixing in $a(1)$, and enters the semi-empirical estimate of the EDM enhancement factor [7]. The difference $\delta g = g_e - g_f$ is important for determining the level at which some systematics in the EDM measurement can be rejected by using the doublet levels as internal co-magnetometers [9].

We extracted g-factors from the changes observed in ν_b corresponding to controlled changes in B-field magnitude. These were determined before and after data-taking in the volume occupied by the cell with a calibrated 3-axis magnetometer. We found $g_e = 1.857(6)$, in agreement with our earlier, less precise measurement [12]. Our precision was limited primarily by uncertainty in the magnetic field calibration, with smaller uncertainties due to magnetic field noise and uncertainties in the fit function. By driving the $Q1$ transition and comparing changes in beat frequencies with the $R0$ results for the same changes in B, the difference in g-factors was determined : $\delta g = -25(13) \times 10^{-4}$. Here the uncertainty is largely immune to the calibration, and comes from equal parts statistical uncertainty and magnetic field noise.

We obtained higher accuracy in δg using a more sophisticated method. As before, we drove the $R0$ transition with $\hat{\mathbf{x}}$ polarized light, creating alignment of the $J = 1^-(e)$ level, and measured $\nu_b \propto g_e$. Periodically, we also created an alignment in the $J = 1^+(f)$ level, so $\nu_b \propto g_f$, in the following manner. Three microseconds after the laser pulse, we applied a pulse of RF electric field at frequency $\nu_{RF} = \Delta_\Omega/h$, to resonantly drive the $\Delta M = 0$ electric dipole transition between the e and f levels (see Fig. 1). The time duration $T_{RF} \approx 5$ μs and amplitude $E_{RF} \approx 0.12$ V/cm of the RF pulse were adjusted to create a π-pulse. This method allows us to switch more rapidly between e and f levels than was possible by tuning the laser between the $R0$ and $Q1$ transitions, and thus eliminates much of the noise due to drifts in ambient B-field during the measurement. Measuring the change in beat frequency between data with or without the RF pulse yields $\delta g = -31(9) \times 10^{-4}$. The error is from uncertainty in the efficiency of the π-pulse transfer, and from the statistical uncertainty in the beat frequency differences. The combined result is $\delta g = -30(8) \times 10^{-4}$, in coarse agreement with predictions.

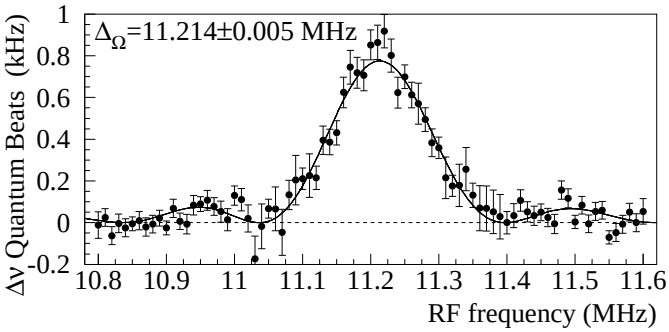

FIG. 3: The change in quantum beat frequency ν_b is shown as a function of the frequency ν_{RF} of an RF π-pulse. A $\pi-$pulse at the frequency of the Ω-doublet splitting transfers population from the e to f levels and changes the beat frequency from $\nu_b \propto g_e B$ to $\nu_b \propto g_f B$.

This difference in g-factors was the basis for an RF-spectroscopic study of the Ω-doublet splitting, by monitoring the change in ν_b as a function of ν_{RF}, as shown in Fig. 3. We found $\Delta_\Omega = 11.214(5)$MHz, where the uncertainty is dominated by possible systematic effects due to off-resonant AC Stark shifts (Bloch-Siegert shift). This is consistent with the best previous measurement [12], but 40 times more precise. We obtain similar results by monitoring the change in beat contrast when driving the $e \to f$ transition. This contrast difference is associated with different angular distributions of fluorescence for the $e \to X(J'' = 0, 2)$ and $f \to X(J'' = 1)$ transitions.

Next we turn to results obtained with a static electric field $\mathbf{E} = E\hat{\mathbf{z}}$. Such a field mixes the e, f sublevels with the same value of M, leading to states of mixed parity separated in energy by $\Delta(E) = \sqrt{\Delta_\Omega^2 + (\mu_{J,M}E)^2}$. Here $\mu_{J,M}$ is the matrix element of the electric dipole opera-

tor $\hat{\mu}$: $\mu_{J,M} = \langle e, J, M|\hat{\mu}|f, J, M\rangle = \mu_a M/J(J+1)$, and μ_a=1.64(3) MHz/(V/cm) is the molecule-fixed dipole moment in the $a(1)$ state [12].

We used the PbO molecules to sense weak applied E-fields (E <2 V/cm), by measuring the Stark shift in the Ω-doublet splitting. As before, we populated the $J = 1^-$ (e) $M = \pm 1$ levels at $E = 0$ by driving the $R0$ transition with $\hat{\mathbf{x}}$ polarized light. Several microseconds after the laser pulse, E was ramped up adiabatically over 2.5 μs ($1/E \cdot dE/dt < \Delta_\Omega/h$), and an RF π-pulse ($\approx$ 5 μs in duration) was applied to the electrodes at $\nu_{RF} = \Delta_\Omega/h$ to drive the $E1$ $\Delta M = 0$ transition to the other state of mixed parity. Then E was ramped down adiabatically and the quantum beat frequency was determined. For ν_{RF} far from resonance, no population is transferred to the lower level, so the beats are characterized by g_e, whereas resonant excitation yields beats characterized by g_f. The observed dependence of the splitting with electric field gives experimental evidence of an electric field in the cell in qualitative agreement with predictions (limited by our knowledge of the relation between applied voltage and E-field in the cell).

This method for determining Stark shifts could not be extended to larger $E-$fields due to technical limitations. However, we observed clear signatures of large E-fields in the cell. For these observations, E was kept on during the laser excitation, which used $\hat{\mathbf{x}}$-polarized light tuned to the $R0$ transition. We observed a minimum in beat lifetime T_2 when the Stark shift approximately matches the Zeeman shift, bringing the $M = -1$ and $M = 0$ levels into degeneracy. Then Majorana spin-flips depopulate the $M = -1$ level and minimize the beat lifetime. Upon increasing E the degeneracy is broken; the beat lifetime recovers and is limited finally by field inhomogeneities. Large E-fields $E \geq h\Delta_\Omega/\mu_a$ should also result in a beat contrast equal to the average of e and f level contrasts, corresponding to a rapidly oscillating coherent superposition of these states. We observed contrasts approaching 80% of this value. We attribute this to difficulties distinguishing changes in contrast from lifetime.

Maximum sensitivity to an EDM requires applying a field large enough to reach electrical polarization $P =< \mathbf{J}_e \cdot \hat{\mathbf{n}} > \approx \pm 1$, corresponding to complete mixing of the Ω-doublet states to form eigenstates of definite Ω [7]. Here P depends on E as $P = 2\alpha\beta/(\alpha^2 + \beta^2)$ where $\alpha = \mu_{J,M}E$, and $\beta = \Delta_\Omega/2 + \sqrt{(\Delta_\Omega/2)^2 + (\mu_{J,M}E)^2}$. We have successfully applied static electric fields $E >$ 50 V/cm to our cell, corresponding to $P \sim 99\%$, with no signs of failure. However, we observed a substantial leakage current in the cell $I_L \approx 1$ μA at $E \approx 50$ V/cm. In the worst case this current can produce a field $B_L \approx 10^{-7}$ G causing beat frequency shifts $\Delta\nu_b \approx \bar{g}\mu_B B_L/h$. The shift changes sign upon reversal of E, and mimics an EDM. We expect to reduce I_L considerably with improved cell design and handling procedures.

A powerful technique for separating the EDM from such systematics comes through comparisons of ν_b observed in the two doublet levels, without the need to reverse fields [9]. Fully mixed upper and lower doublet levels have opposite orientations of the internal electric field and exhibit opposite shifts due to an EDM. Systematic shifts retain the same sign and magnitude to the extent that the effective g-factors of the mixed doublet levels are the same. Thus in the limit of nearly complete mixing $\mu_a E \gg h\Delta_\Omega$, leakage currents change ν_B between doublet levels by only $\Delta\nu_b \approx \delta g \mu_B B_L[\Delta_\Omega/(h\mu_a E)]$, suppressing the systematic shift due to B_L by $\gg 10^3$, and allowing a systematic limit $\lesssim 10^{-29}$ e·cm.

In conclusion, we have demonstrated the feasibility of a new approach to measuring the electric dipole moment of the electron in the metastable $a(1)\left[^3\Sigma^+\right]$ state of PbO. With our present configuration, it is feasible to achieve EDM sensitivity comparable to the current limit [2]. However, the sensitivity can be improved dramatically with straightforward modifications. In particular: by using two photodiodes with high quantum efficiency instead of a single PMT, exciting from the $X(0)(\nu'' = 0)$ level, using broad band interference filters to capture the fluorescence into two vibrational levels simultaneously, using isotopically enriched ^{208}PbO, and other improvements, we expect to increase the count rate by more than three orders of magnitude, and the contrast by more than a factor of two. These changes should result in a statistical sensitivity approaching 100 mHz/$\sqrt{\text{Hz}}$. From the theoretical estimates of the enhancement factor [7, 8], a statistical limit at the level of $|d_e| \sim 10^{-29}$ e·cm will be achieved in less than a month of integration. The necessary modifications are now underway.

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