

Spectroscopy of laser-ablated buffer-gas-cooled PbO at 4 K and the prospects for measuring the electric dipole moment of the electron

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We demonstrate production of cold lead monoxide (PbO) molecules by laser ablation in a cryogenic cell filled with helium buffer gas and cooled by a cryostat to a temperature of 4 K. The molecules are probed by laser-induced fluorescence excited in the $X \rightarrow B$ band. The molecules thermalize with the buffer gas, both translationally and rotationally, in less than 30 ms after the ablation pulse. A single ablation pulse fired at the solid PbO sample yields about 10^{12} cold molecules. We present an analysis indicating that buffer-gas cooled PbO molecules excited to either the a or B state could be effectively used to search for the permanent electric dipole moment of the electron.

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The search in progress for the electric dipole moment of the electron is a crucial test of time reversal symmetry that could shed light on the baryon asymmetry of the universe [1]. Currently, the experimental upper bound on a possible permanent electric dipole moment (EDM) of the electron is about $4 \times 10^{-27} e \text{ cm}$ (i.e., $1.6 \times 10^{-18} \text{ D}$) [2], sufficient to narrow the range of theoretical contenders for particle physics beyond the standard model [3]. Improving the bound by tenfold or more is a prospect and would provide a much more stringent test of theoretical predictions. Some of the promising experimental approaches employ molecules [4–6]. Within molecules containing a high- Z atom, such as YbF [7] or PbO [8], an unpaired electron is subject to a huge effective internal electric field, of the order 10 GV/cm [10,11]. The EDM experiment requires spatially polarizing the electron spin and also orienting the huge internal field. The internal electric field can be oriented in the laboratory frame by orienting the molecular axis. An interferometric technique can then be used to search for tiny frequency shifts associated with reversing the field directions; see, e.g., [6].

The orientation of the molecular axis is characterized by $\langle \cos \theta \rangle$, the expectation value of the cosine of the polar angle θ between the molecular axis and the external electric field. In the EDM search it is desirable to have the largest feasible magnitude for $\langle \cos \theta \rangle$. This can be attained either by making the molecules pendular in a strong field (typically of about 10 kV/cm), or, in the case of symmetric top molecules or equivalent, by exploiting the first-order Stark effect (the requisite field strength can be as low as 1 V/cm [9]). Sizable values of $\langle \cos \theta \rangle$ can be readily attained for the low rotational levels. However, in the molecular beam [7] or vapor cell [8] techniques so far used these levels are sparsely populated. Also, the thermal velocities of the molecules limit the time available to produce observable interferometric phase shifts. Cooling the molecules could thus greatly enhance the EDM experiment.

Recently, we developed a technique of cooling molecules for both trapping [12] and spectroscopy [13]. This technique, *buffer-gas cooling* [14], relies on thermalization of the species to be cooled via collisions with a cold buffer gas that is

maintained, in turn, by a cryogenic device. The buffer gas serves to dissipate both the translational and internal energy of the molecules. At temperatures of ~ 1 K, all stable substances except for He have negligible vapor pressure. We found that laser ablation represents a means to bring the species to be cooled into the gas phase within the cryogenic environment. It is also possible to “prepare” molecules, of varying complexity, by ablating a suitable precursor [15]. Another technique of introducing gases into the cryogenic environment is being developed in our laboratory, the coupling of a molecular beam to the cryogenic cell.

Both in a vapor cell and in a buffer gas only low electric fields (of up to about 30 V/cm) can be applied without causing an electric discharge [16]. Therefore, in these types of experiment molecular orientation by the first-order Stark effect is assumed to be the only option. This, in turn, limits the electronic states considered for such experiments to those that belong to Hund’s cases (a) or (c), usually found among the electronically excited states of linear molecules.

We also note that a $^{2S+1}\Sigma$ state (with $S \geq \frac{1}{2}$), which frequently occurs in ground electronic states, can also be oriented using a weak electric field. This is achieved by combining such an electric field with a magnetic field in a process dubbed steric proficiency [17,18]. In a magnetic field, various pairs of Zeeman states with opposite parity become degenerate (i.e., they cross) at certain values of the magnetic field. Introducing even a weak electric field connects such states, producing a first-order Stark effect that then markedly sharpens the orientation of the molecule.

In this paper we report an experiment that demonstrates the production of PbO molecules by laser ablation and their thermalization with a cold He buffer gas. The molecules were detected by time-resolved laser-induced fluorescence spectroscopy in the $B \rightarrow X$ band and their translational and rotational temperatures were determined. The molecules were found to thermalize with the buffer gas, maintained at 4.2 K by a He cryostat, on a millisecond time scale (about 100 elastic PbO-He collisions for an assumed initial temperature of 1000 K suffice to cool PbO [12]). About 10^{12} thermalized PbO ($X^1\Sigma, v''=0$) molecules were produced by

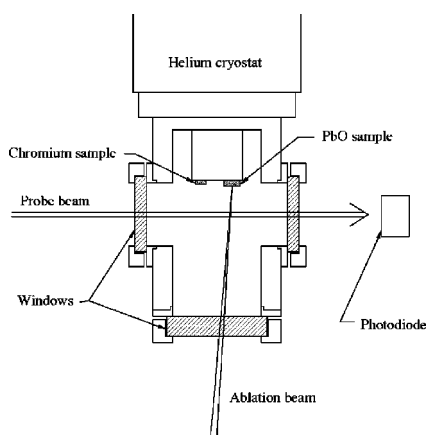


FIG. 1. A view of the cryogenic apparatus.

a single pulse of the ablation laser and their population was found to decay, mainly by diffusion towards the cell walls, with a lifetime of about 20 ms. Below we present an analysis indicating that the EDM search could be done in the cryogenic cell either with the *a* or *B* state of PbO, and that the statistical advantage of using the *a* state would shorten the integration time by between two and three orders of magnitude compared with the *B* state. Nevertheless, reducing the upper bound on the electron's EDM to $10^{-29}e$ cm (neglecting systematic considerations) seems within reach even using the *B* state by decreasing the cell's temperature to about 0.5 K.

Our experimental setup consists of four main parts: a cryogenic cell with optical access, a He cryostat to which the cell is anchored, an ablation laser, and a probe laser system with an optical detector. Figure 1 shows the cell along with the ablation and probe laser paths.

The cell, made out of brass, is of cylindrical shape with an outer diameter of 6 cm and 10 cm long. It has a five-way optical access through windows made out of BK7. The cell is filled with the ^4He buffer gas and holds a PbO target (see description of target below). The cell is attached to a liquid-helium cryostat that maintains it at 4.2 K. A stainless-steel shield (not shown), equipped with BK7 windows, is connected to a liquid-nitrogen dewar and protects the cryostat and the cell from room-temperature thermal radiation. A stainless-steel tube of 2 mm diameter connects the cell with a gas handling system (not shown). The number density of the He buffer gas was maintained in the range between $2-3 \times 10^{16} \text{ cm}^{-3}$ by periodically adding gas to the cell's volume (of about 150 cm^3). Helium was "lost" on a time scale of many hours. Based on changes of loss rate with time and pressure changes during ablation we attribute this loss to adsorption by the ablation targets. The helium was released after the cell was warmed up.

The target was ablated with a 532 nm pulsed laser, with a pulse duration of 5 ns and a typical energy of 25 mJ per pulse focused to a waist of about $100 \mu\text{m}$, yielding an intensity of about 10^{10} W/cm^2 . The repetition rate of 2.5 Hz was limited by the performance of our shutter (see below).

The sample ultimately used was a vacuum hot-pressed disk, about 1 cm in diameter and 3 mm high [19] with the

lead and oxygen isotopes present presumably in their natural abundances. Initially, we were preparing samples by compressing PbO powder at room temperature. Such targets released dust when ablated, necessitating re-aiming at a new spot every 1000 pulses in order to ensure a steady yield of gaseous PbO. The vacuum-hot-pressed targets released no visible dust and the ablation yield remained steady over about 10^{5-6} ablation pulses aimed at the same spot. The yield remains consistent from spot to spot.

The ablation pulse creates a plasma glow. The fluorescence detector had to be shielded from this glow (see below). It was noticed with the vacuum hot-pressed sample that when the ablation laser was aimed at a fresh spot the plasma glow was maximal. Over several thousand pulses it decreased to about 10% of its maximal level. Sometimes, during a measurement, an order of magnitude increase in glow level occurred and disappeared again after several thousand pulses. We attribute this effect to changes in the surface properties of the sample due to the ablation. The glow intensity also showed pulse-to-pulse fluctuations, but the number of molecules detected remained steady, with no apparent relation to the level of the glow.

The molecules released into the gas phase by the ablation pulse were probed by laser-induced fluorescence excited in the $X(0) \rightarrow B(v')$ bands at either 441 nm ($v'=1$) or 432 nm ($v'=2$) and detected in the $B(v') \rightarrow X(v'')$ bands, either with $v'=2, v''=3$ at 475 nm or with $v'=1, v''=6$ at 541 nm.

The probe beam was produced by frequency doubling the output of an actively stabilized Ti:sapphire ring laser in a lithium triborate crystal cavity. The resulting beam with a typical power of 10 mW was acousto-optically modulated at 15 kHz, passed horizontally through the central region of the cell, and monitored by a silicon photodiode. A photomultiplier tube (PMT), placed perpendicular to both the ablation and probe beams, was protected from high light levels arising from the ablation pulse and the early plasma glow by a mechanical shutter and by gating the PMT's base. The PMT was exposed to light only during times between 30 and 150 ms after the ablation pulse. Since the plasma glow intensity goes down much faster than the density of PbO molecules, opening the gate with the 30-ms delay allowed us to cut down significantly the noise from the background light. Band-pass interference filters in front of the PMT further reduced the background from the glow as well as from the scattered probe beam. The photomultiplier was used in the current mode, and its output was fed into a lock-in amplifier. The resulting signal was normalized by the reference laser power monitored by the photodiode. The laser-induced fluorescence spectra were measured over a range of 7 cm^{-1} in stretches of 0.3 cm^{-1} . Within each stretch, the laser was scanned in steps of 20 MHz. In order to determine the line profile, the step size was reduced to 10 MHz. The probe-laser frequency was measured with a wavemeter (Burleigh W-20). The PbO fluorescence was calibrated using chromium atoms as a standard. A chromium sample, also placed in the cell, was ablated and the signal from the $^7S_3 \rightarrow ^7P_3$ transition at 427 nm was observed in both absorption and fluorescence [20].

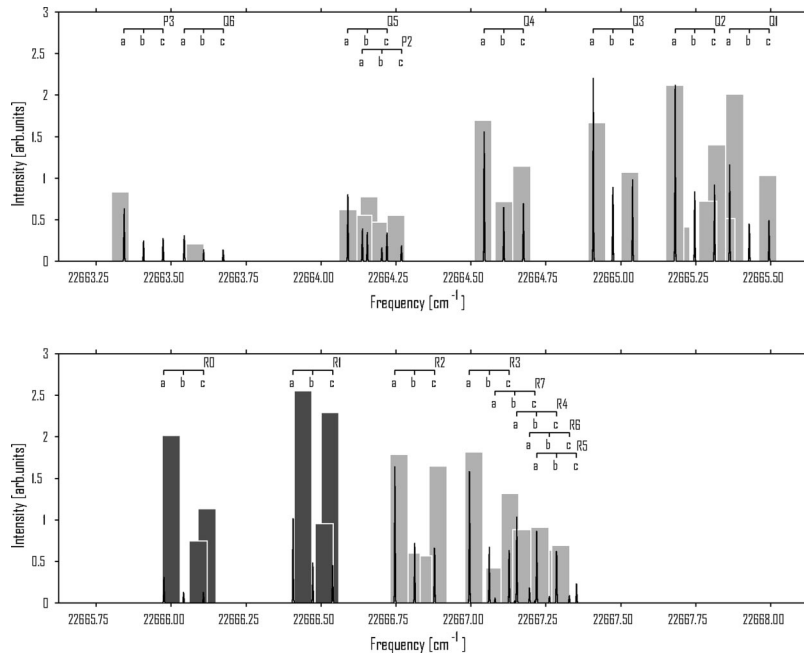


FIG. 2. The fluorescence spectrum excited in the $X(0) \rightarrow B(1)$ band at 441 nm and detected in the $B(1) \rightarrow X(6)$ band at 541 nm. The shaded bars show the measured spectrum, the Gaussians the simulation. Transitions due to $^{208}\text{Pb}^{16}\text{O}$, $^{207}\text{Pb}^{16}\text{O}$, and $^{206}\text{Pb}^{16}\text{O}$, are labeled as a , b , and c , respectively. The laser frequency scale has been calibrated by our wavemeter. See also text.

Figure 2 shows the fluorescence spectra excited in the $X(0) \rightarrow B(1)$ band at 441 nm and detected in the $B(1) \rightarrow X(6)$ band at 541 nm. The shaded bars show the measured spectrum. The width of the bars represents the error in determining the transition frequency (about ± 1 GHz). The error in determining the relative line intensity was about $\pm 30\%$. The dark-shaded bars correspond to data obtained under different experimental conditions than the rest. The inaccuracies arise predominantly from the manual scan of the probe laser and the corresponding lack of control of its frequency. The accuracy of our spectroscopic measurements could be dramatically improved by scanning the laser continuously, as was done in our earlier work [12]. Also shown is a simulated spectrum based on molecular constants of Martin *et al.* [21]. The lines in the calculated spectrum are represented by Gaussians whose positions and heights correspond to the energies, $(E' - E'')/(hc)$, and intensities, $I_{J''} = w_{J''} S_{J'' \rightarrow J'}$, with $S_{J'' \rightarrow J'}$ the line strengths [23], and $w_{J''} = (2J'' + 1) \exp[-J''(J'' + 1)B''/kT]/Q$ the Boltzmann factors; here Q is the rotational partition function, k the Boltzmann constant, and T the temperature.

The width of the lines was measured to be 80 ± 20 MHz, which is consistent with a Doppler broadening at a translational temperature of 4 ± 1 K. From the intensity distribution of the lines the rotational temperature was determined to be likewise 4 ± 1 K. The molecules were found to thermalize with the buffer gas on a time scale of less than 30 ms. Adding buffer gas into the cell was found to extend the lifetime of the PbO molecules, indicating a diffusion-limited loss process [13].

The simulated spectrum agrees well with the measured one and provides an assignment of the observed transitions. The $^{207}\text{Pb}^{16}\text{O}$ isotope possesses a hyperfine structure due to the magnetic dipole moment of the ^{207}Pb nucleus [22]. This was not resolved in the spectrum and was omitted from the simulation. As can be seen in Fig. 2, the bandhead region of the spectrum is solely due to an R branch, which is followed

by a sparse Q branch toward longer wavelengths. Also several P -branch transitions were detected. The most populated rotational state is the one with $J'' = 2$. All the transitions occur in “triplets,” due to the presence of the three isotopic variants of PbO; it is the different vibrational frequencies that are mainly responsible for the observed frequency shifts within a given “triplet.” The assignment of the lines in the spectrum according to the isotopic variant of PbO is also indicated. In the spectral range covered (7 cm^{-1}) all transitions were found to be due to the $B-X$ band of the PbO molecule only. With the aid of a calibration based on the absorption and fluorescence of laser-ablated Cr atoms, we determined the number of the thermalized PbO molecules following a single ablation pulse to be $N = 10^{12}$. We hope to improve our ablation production yield by a factor of 10–100. This might be further enhanced by coupling a molecular beam of PbO to the He cryogenic cell.

Based on these results, the prospects of using buffer-gas cooled PbO in the EDM search are promising. From the measured lifetime of the molecules in the cell, we estimate the collision time within the He buffer gas (at a number density $n \approx 10^{16} \text{ cm}^{-3}$ at 4 K) to be on the order of $1 \mu\text{s}$. If collisions with the He gas limit the coherence time of the EDM measurement to a microsecond time scale, then there may be no appreciable disadvantage to using the B state of PbO whose radiative lifetime has been measured to be $\tau = 3 \mu\text{s}$ [8]. For the actual EDM experiment it should be possible to set up the necessary coherent superposition of molecular spin states in less than a microsecond using pulsed excitation [6]. However, since spin decoherence may require many collisions, it is possible that the $a^3\Sigma^+$ state (with a natural lifetime of $80 \mu\text{s}$ [8]), singled out for the vapor cell experiment by DeMille *et al.* [8], may also prove usable in the buffer-gas cell. The B state is, in Hund’s case (a) notation, a $^3\Pi_1$ state with a small Ω doubling [21]. Thus its symmetric top states with J , M , and Ω all nonzero can be oriented by an electric field of a few V/cm. For either the a

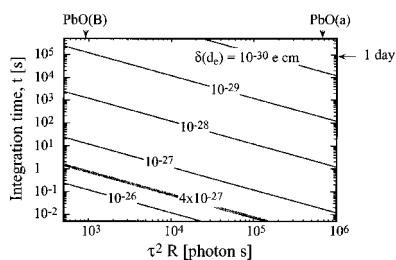


FIG. 3. A nomogram for the values of the integration time and of the product $\tau^2 R$ that are required in order to attain a given statistical sensitivity $\delta(d_e)$ for a given upper bound on electron's EDM d_e . The arrows on the upper abscissa indicate the values of the $\tau^2 R$ product for the a and B states of PbO at a cell temperature of 0.5 K. Also indicated (gray line) is the current value of the upper of d_e , Ref. [2].

or B state, we assume $R(0)$ to be the probed transition. The internal electric field within the PbO(B) molecule can be expected to be similar to the one in PnO(a). The electric breakdown in the buffer-gas cell is likely to occur at an electric field of about 30 V/cm [16], much greater than the field needed for orientation.

We now evaluate the statistical sensitivity of the EDM measurement. We follow the analysis (and use most of the notation) of DeMille *et al.* [8]. We begin by considering the photon count rate for the experiment. Once a PbO molecule is excited, it will likely decay to a different vibrational level, and cross sections for vibrational relaxation at ≈ 1 K are typically extremely small [13,24]. Because of this, we assume that each PbO molecule can only be excited once in the proposed experiment. Our photon count rate R is thus limited to $R = \varepsilon_e \varepsilon_d \dot{N}_0$, with ε_e and ε_d the excitation and detection

efficiencies and \dot{N}_0 the rate at which ground-state molecules are produced. The ground-state production rate is given by $\dot{N}_0 = w_0 \dot{N}$, where \dot{N} is the total production rate of the molecules and w_0 the population of the ground rotational state. Since $w_0 = 1/Q \approx B''/(kT)$ (a good approximation down to $kT \approx B''$), we have $R = \varepsilon_e \varepsilon_d \dot{N} B''/(kT)$.

Due to the large oscillator strength of the $B-X$ transition, it should be straightforward to achieve $\varepsilon_e \approx 1$ with standard pulsed laser systems. Assuming $\varepsilon_d \approx 0.1$ and $\dot{N} \approx 10^{15}$ Hz, we finally have $R \approx 10^{14}$ Hz at 0.5 K. The photon count rate for the a state may be somewhat lower, due to the reduced oscillator strength of the $a-X$ transition. However, for the same photon scattering rate, the attainable energy resolution, $\delta(\Delta E)$, should be higher for the a state since $\delta(\Delta E) = \hbar/[\tau(tR)^{1/2}]$, where t is the integration time (i.e., time of the measurement). The nomogram of Fig. 3 shows the values of the integration time and of the product $\tau^2 R$ that are required in order to attain a given statistical sensitivity for a given upper bound on d_e , the electron's EDM (we assume $\Delta E = |d_e \varepsilon_{\text{eff}}|$ with $\varepsilon_{\text{eff}} = 6$ GV/cm, the effective electric field strength inside the molecule [8], and take $R \approx 10^{14}$ Hz). The arrows on the upper abscissa indicate the values of the $\tau^2 R$ product for the a and B states of PbO at a cell temperature of 0.5 K. Although the integration times are about 2–3 orders of magnitude greater for the measurements with the B state compared with the a state, reaching $\delta(d_e)$ of $10^{-29} e$ cm with the B state could be feasible (one day of integration), yielding a hundredfold improvement over the current value.

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