1: Final Report DE-FG02-07ER46361 The University of Oklahoma
2: **Ro-vibrational Relaxation Dynamics of PbF Molecules**

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3: April 8, 2011 (Covering budget period 1/1/2008 - 1/31/2011, \$433,959)

4: Participating Laboratory: Brookhaven National Laboratory (Gregory Hall and Trevor Sears)

I. 5) GOALS AND OBJECTIVES

In 1950 Purcell and Ramsey[1] suggested that the electron might have a CP-violating electric dipole moment (e-EDM) proportional to its spin angular momentum. This possibility initiated an ongoing hunt for the e-EDM that has been spurred on by the recognition of the importance of CP-violation to the formation of a matter-dominated universe[2] as well as a difference in magnitude of the Supersymmetric[3] and Standard Model[4] prediction for its value. The current limit on the e-EDM is 1.6×10^{-27} e-cm as determined in a Ramsey beam resonance study of the Tl atom[5].

The PbF molecule provides a unique opportunity to measure the e-EDM. The molecule's odd electron, heavy mass, and large internal field combine to give it an intrinsic sensitivity to an e-EDM that is over three orders of magnitude bigger than that of the Tl atom[6]. In addition to this increased intrinsic sensitivity, the ground state of the PbF molecule allows for a "magic" electric field at which the magnetic moment vanishes[7]. All of these advantages create an opportunity to significantly lower the current limit on the e-EDM. These advantages can only be realized if an intense source of ground-state PbF molecules can be created and detected with high efficiency. The scope of this project is to (1) create a rotationally cold molecular beam source of PbF, (2) achieve a continuous ionization scheme for sensitive state selective detection of the PbF molecule.

II. 6) ACCOMPLISHMENTS

This research effort has been supported by the DOE since January of 2007. It has supported two years of Ph.D. work by graduate student Milinda Rupasinghe and four years of Ph.D. research support for graduate student Christopher McRaven. In addition, three publications. In addition, it resulted in four publications. The details of results posted in each of these publications are given below:

2.1) The Effect of the Geometric Phase on the Possible Measurement of the Electron's Electric Dipole Moment Using Molecules Confined by a Stark-Gravitational Trap, Milinda Rupasinghe, N.E. Shafer-Ray, Phys. Rev. A, 78 033427 (2008)

It is possible to envision a molecular $e - EDM$ experiment which probes PbF molecules confined to a region in space by a non-uniform electric field, as illustrated in Fig 2.1. In such an experiment, one would polarize the trapped molecules creating a coherent superposition of

states differing only in the sign of the projection of total angular momentum onto an electric field axis. If the electron were to have an electric dipole moment (i.e., if an $e - EDM$ exists) then these two states would have different energies and evolve creating a measurable time-dependent quantum beat.

FIG 2.1: Electrodes that could be used to create a trap which confine PbF molecules in a potential created by the Earth's gravitational field and an anisotropic electric field.

FIG 2.2: Energy level structure of $^{208}\text{Pb}^{19}\text{F}$ molecules confined to the Stark-gravitation trap of FIG 2.1.

The original aim of our previously funded DOE research was to investigate the rotational-relaxation dynamics of a hot source of PbF in a cold bath of He. If these dynamics were to be favorable, it would allow us to produce a sub-Kelvin source of molecules that could be loaded into a trap. We soon realized, however, that to perform an $e - EDM$ experiment would require more than just a trapped population of PbF. Specifically, the $e - EDM$ measurement would be limited by a coherence time τ that is much shorter than the lifetime of molecules in the trap. Instead τ would be determined a geometric phase effect that couples the angular momentum of the center-of-mass motion of a molecule to its internal angular momentum.

In this work we used the formalism of Longuet-Higgins[8] to derive an effective Hamiltonian for this effect and determined the coherence time τ . Specifically we find that geometric phase couples the center-of-mass motion of a trapped molecule to its internal angular momentum via the effective Hamiltonian

$$\Omega_{geo}(\vec{r}) = \frac{2m\hbar i}{M} \sum_{n=1}^3 \left[\left(\left(\nabla_n \frac{\vec{e}}{e} \right) \times \frac{\vec{e}}{e} \right) \cdot \hat{z} \right] \nabla_n.$$

Here m is the projection of the molecule's internal angular momentum on the electric field axis, M is the mass of the molecule, $\vec{r}$ is the position of the molecule in the trap, $\nabla_n \in \{\partial_x, \partial_y, \partial_z\}$ and $\vec{e} = \hat{z} + \hat{E}$ is the sum of the unit vectors giving the direction of the laboratory frame axis and direction of the electric field. Because the expectation value of $\Omega_{geo}(\vec{r})$ over the center-of-mass wave functions of the trapped molecules is not zero, the $\pm m$ degeneracy expected by CP symmetry is lifted.

The expected energy level structure of a molecule trapped in a Stark gravitational trap is shown in Fig 2.2. Rotational and hyperfine energies are expected to be much greater than the trap energies which are typically of order 1 Hz. The Geometric Phase effect further splits these energy levels. It is interesting to note that the trap still exhibits a degeneracy

between states which differ only by the sign of the total (internal plus center-of-mass) angular momentum.

If one could create a cloud of molecules so cold that coherent superpositions of two center-of-mass states could be made, the geometric-phase induced-level structure could actually be useful, providing a well-understood energy level structure of comparable size to the e -EDM effect. However, such extraordinary control over the center-of-mass motion is currently limited to the alkali atoms. For the experiment we visualize, the geometric phase effect simply limits the coherence time of an e -EDM experiment to $\tau \approx \left[\frac{T}{23mK}\right]^{-2}$ sec. This is an unfortunate result because our proposed cooling techniques do not produce a population of PbF molecules in the mK temperature range. Thus even if successful in cooling and trapping PbF molecules, our coherence time would not exceed that of a molecular beam experiment. For this reason, a change in direction of the research project was requested and granted by the DOE. Specifically, our effort was shifted to the development of continuous resonance-enhanced multiphoton ionization detection scheme.

2.2) *Characterization of the X_1 , A , B , D , E , $E1$, and $F1$, and F states of PbF.* *J Mol Spec*, 262, 89 (2010.)

Fig 2.3: 2-D spectra of rotationally-resolved $X_1(v=0) \rightarrow A(v=1) \rightarrow D(v=0)$ transitions of PbF.

We have completed a detailed spectroscopic study of all known electronic states of the PbF molecule except the C state (which we can not detect with rotational-state resolution.) These states were detected with 2-dimensional resonance-enhanced multiphoton ionization via the process $X_1^2\Pi_{1/2} \rightarrow A^2\Sigma_{1/2} \rightarrow [B(v=0), D(v=0), E(v=0,1), \text{ or } F(v=0,1)] \rightarrow PbF^+$. Typical data spectrum are shown in Fig. 2.3. With this REMPI scheme, we have corrected values of T_e by as much as 100 cm^{-1} , we have determined heretofore unknown rotational constants, we have assigned term symbols to the C and D states, and determined the value of Ω for the E and F states. We have also

confirmed the parity of the B state. One interesting finding is that the assumed electronic mixing of the X_1 , X_2 , and A states is not as simple as once thought. In a simple three-state $^2\Pi_{1/2} - ^2\Pi_{3/2} - ^2\Sigma_{1/2}$ mixing scheme, the sum of the ratio of omega-doubling constant to rotational constant p/B is ± 2 (see [6, 9].) These ratios are given in the table below for the X_1 , A , and D states.

	$X_1(v=0)$	$A(v=7)$	$A(v=0)$	$D(v=0)$
p/β	-0.605	2.60	2.996	-1.04

(1)

This table, as well as the energy levels of the electronic states suggest that the $X_1^2\Pi_{1/2}$, $X_2^2\Pi_{3/2} \rightarrow A^2\Sigma_{1/2}(v=7)$ system forms one strongly mixed $^2\Pi - ^2\Sigma$ system whereas the $D^2\Pi_{1/2}$, $C^2\Pi_{3/2} \rightarrow A^2\Sigma_{1/2}(v=0)$ forms another. In light of this finding, a re-evaluation of the sensitivity of the molecule's sensitivity to parity violation is needed.

2.3) *Direct measurement of the lifetime of the D state of PbF*, P. Sivakumar, C.P. McRaven, Dustin Combs, N.E. Shafer-Ray, and Victor Ezhov, *Phys. Rev. A* 77, 062508 (2008.)

Fig 2.4: Time-dependent decay of the D state of PbF.

doubly resonance enhanced ionization scheme

Knowledge of the D -state lifetime is critical to the design of an optimal laser system to implement this ionization scheme. Unfortunately the bandwidth of the Nd:YAG pumped dye laser system used to discover the $A \rightarrow D \rightarrow PbF^+$ ionization pathway is not sufficiently narrow to make a conclusive statement about the D -state lifetime. For this reason we coaxed our 7-ns Nd:YAG laser system to perform a time domain measurement with picosecond resolution. To accomplish this we took advantage of the temporal mode structure of our unseeded Nd:YAG laser-pumped dye laser system. This structure is observed in an auto-correlation measurement that monitors the 251-nm radiation resulting from sum-frequency generation of 532-nm and 477-nm laser radiation in a BBO crystal as a function of an optical delay between the two input wavelengths. Determination of the lifetime of the D state of PbF is made by observing the PbF^+ ionization signal as a function of the delay between the 477-nm and 532-nm laser radiation. The resulting time-dependent ionization signal (Figure 1) indicates a lifetime of 250 ± 150 ps. The D -state lifetime is short enough to dramatically reduce the efficiency of an ionization scheme utilizing continuous wave radiation. For this reason, we employ a pseudo-continuous source of laser radiation (see section 2.4.)

2.4) *Observation of continuous ionization of the PbF molecule*, *Mol Phys*, 28, 927 (2011)

The combination of mass discrimination and near-unit quantum efficiency for detection makes Resonance Enhanced Multiphoton Ionization (REMPI) one of the most sensitive molecular detection techniques[?]. However, although the technique has a very high peak sensitivity, it is typically carried out with nanosecond pulsed laser systems which operate at

10 to 10,000 Hz repetition rate. These pulsed laser systems have two disadvantages. The first disadvantage is a very low effective duty cycle. This duty cycle is given by the ratio of time it takes for molecules to cross the laser radiation (typically microseconds) to the time between pulses of laser radiation (typically 0.1 to 100 ms.) Thus a factor between 100 and 10^4 in data collection rate is lost. A second disadvantage is that pulsed laser systems often have limited resolution given, in the best of circumstances, by the Fourier transform of the time-dependence of the radiation pulse.

Figure 2.5: Hyperfine resolved pseudo continuous ionization spectra of The $X_1 \rightarrow A$ transition of the three common isotopes of PbF

figure 1

Fortunately a new generation of easy to use picosecond OPO systems have been developed (largely to aid in CARS spectroscopy.) These pseudo continuous systems produce broadly tunable picosecond pulses of laser radiation at a repetition rate of typically 50-100MHz. This rate is sufficiently fast that, even for the case of a tightly focussed beam, molecules are exposed to several pulses of radiation before drifting out of the probe region. By copropagating this radiation with cw laser radiation, one can create state-selective ionization radiation that oc-

curs with high probability each time a molecule enters the probe region. Here we have implemented such an ultra-sensitive cw-REMPI scheme to detect the PbF molecule.

Our ionization scheme begins with a blue diode laser (Toptica DL100) that produces 10 mW of radiation at 437 nm. This radiation is used to excite the $X_1(v=0) \rightarrow A(v=1)$ transition. The second harmonic output of a Nd:YVO₄ laser (High-q laser picoTrain) is then used to pump an OPO system (APX Levante Emerald) to produce 1.4 watts of 863 nm laser radiation which arrives in 6 ps pulses at a repetition rate of 76 MHz. The Nd:YVO₄ harmonic separation optics have been modified to access the residual 1064 nm from the SHG crystal internal to the laser. This residual laser radiation (3.0 watts) is mixed in an type II SFG LBO crystal (Red Optronics) to produce 700 mW of 476 nm light.

The co-propagating 437 nm and 476 nm laser radiation is tightly focussed onto the molecular beam. The 476 nm laser radiation both excites the $A(v=1) \rightarrow D(v=0)$ transition and ionizes the D state. The PbF⁺ ions are accelerated to a microchannel plate detector. Because the time-of flight of the PbF molecules (1 μ sec) is much longer than the 0.013 μ sec repetition period of the OPO, it is not practical to use the laser pulse as a trigger signal. Instead a symmetric electron detector has been built and is placed opposite to the ion detector. By detecting the electron in coincidence with the ion, mass resolution can be obtained. Both the electron and ion detectors are identical with roles that can be reversed by simply changing the bias voltages. Figure 2.5 shows a spectra that demonstrates the sensitivity of the technique. These spectra are taken from a rotational hot ($T_{rot} = 1400$ K) effusive beam. Nevertheless, individual hyperfine transitions are clearly resolved. The circled transitions

are Q-branch transition from the ground $J=1/2$ level of $^{208}\text{Pb}^{19}\text{F}$. The cw-REMPI scheme we have implemented currently represents a roughly 50-fold improvement in data collection rate and a 10-fold improvement in the spectral resolution achieved by seeding our 10Hz Nd:YAG pumped dye laser system with a diode laser.. Optimization is continuing and we are confident that this technology could be improved to create even more dramatic increases in sensitivity, both to PbF and to other systems. Even the 50-fold improvement in sensitivity we have already observed could have a profound impact on a number of applications that require the ultra-sensitive detection of atoms and molecules.

III. 7) PUBLICATIONS ACKNOWLEDGING THIS GRANT

1. *The Effect of the Geometric Phase on the Possible Measurement of the Electron's Electric Dipole Moment Using Molecules Confined by a Stark-Graviational Trap*, Milinda Rupasinghe, N.E. Shafer-Ray, *Phys. Rev. A*, 78 033427 (2008)
2. *Direct measurement of the lifetime of the D state of PbF*, P. Sivakumar, C.P. McRaven, Dustin Combs, N.E. Shafer-Ray, and Victor Ezhov, *Phys. Rev. A* 77, 062508 (2008.)
3. *Characterization of the X_1 , A, B, D, E, E1, and F1, and F states of PbF*. *J Mol Spec*, 262, 89 (2010.)
4. *Observation of continuous ionization of the PbF molecule*, *Mol Phys*, 28, 927 (2011)

IV. 8) PERSONNEL SUPPORTED UNDER THIS GRANT

The primary mover and shaker on this grant was Christopher McRaven, who's Ph.D. thesis included a large part of the development of pseudo-continuous resonance enhanced multi-photon ionization, the major accomplishment of this grant. Other undergraduate and graduate students floated into and out of the grant as tasks needed to be accomplished that required extra effort.

		months of support ¹					
status	name	07	08	09	10	11	total
undergraduate	Leah Trafford	2	1	-	-	-	3
undergraduate	Jacob Stinnet	-	-	2	-	-	2
graduate student	Prayanka Rupasinghe	1	4	-	-	-	5
graduate student	Sivakumar Poopalasingam	-	4	-	-	-	4
graduate student	Christopher McRaven	-	8	5	12	3	28
graduate student	Tao Yang	-	-	1	-	-	1
graduate student	Haoquan Fan	-	-	-	-	1	1
PI	Neil Shafer-Ray	1	1	1	-	-	3

¹While supported by the DOE, these students worked on projects solely related to this grant. Funding was switched to other grants for portions of their work not related to the DOE project.

V. 9) OTHER SUPPORT

The researcher supported under this grant has led to a newly sensitive detection scheme with what could be profound implications for many applications requiring ultra-sensitive detection of gas-phase molecules. The research results are now being used for an e -EDM measurement supported by the NSF (NSF-PHY0602490.)

VI. 10) COST STATUS

See attached documentation.

University of Oklahoma Norman Campus
Office of Research Services
Department Status Report

Fund Code 50070
Department Number 105053400
Actual Costs as of 3/31/2011
Commitments as of 4/13/2011

CLOSED

Title

Ro-vibrational Relaxation Dynamics of PbF Molecules

Principal Investigator	Professor Neil Shafer-Ray	Agency	US-DOE
Department	Physics & Astronomy	Document No.	DE-FG02-07ER46361
College	Arts & Sciences	Federal Flow-Thru Funds	No
		Type of Award	Cost Reimbursable
		Budget Period	02/01/2009 - 01/31/2011
		Project Period	02/01/2007 - 01/31/2011

Budget Categories	Current Operating Budget	March-11 Costs	Cumulative Costs	Commitments	Uncommitted Balance
Modified Total Direct Cost (MTDC)					
Salaries & Wages	\$104,237.14	\$0.00	\$104,237.14	\$0.00	\$0.00
Fringe Benefits	\$11,883.02	\$0.00	\$11,883.02	\$0.00	(\$0.00)
Project Materials	\$43,850.32	\$0.00	\$43,850.32	\$0.00	\$0.00
Domestic Travel	\$21,781.49	\$0.00	\$21,781.49	\$0.00	(\$0.00)
Foreign Travel	\$5,271.03	\$0.00	\$5,271.03	\$0.00	\$0.00
Professional Services	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00
Technical Meetings	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00
Other Direct Costs	\$6,520.80	\$0.00	\$6,520.80	\$0.00	(\$0.00)
Subtotal: MTDC	\$193,543.80	\$0.00	\$193,543.80	\$0.00	\$0.00
Non-MTDC					
Equipment	\$121,390.73	\$0.00	\$121,390.73	\$0.00	\$0.00
Fabricated Equipment	\$16,619.93	\$936.32	\$16,619.93	\$0.00	\$0.00
Tuition Rate	\$9,503.50	\$0.00	\$9,503.50	\$0.00	\$0.00
Subtotal: Non-MTDC	\$147,514.16	\$936.32	\$147,514.16	\$0.00	\$0.00
Total Direct Cost (TDC)	\$341,057.96	\$936.32	\$341,057.96	\$0.00	\$0.00
F&A Costs @ 48% MTDC	\$92,901.04	\$0.00	\$92,901.04	\$0.00	(\$0.00)
Total Costs	\$433,959.00	\$936.32	\$433,959.00	\$0.00	(\$0.00)

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Report ID: OUGL0010
Bus. Unit: NORM--
Fiscal Year 2011 Period 9
Currency USD

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GRANT INCEPTION-TO-DATE REPORT

Page No. 63
Run Date 04/01/2011
Run Time 09:50:10

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50070 DOE/ARGONNE
105053400 DYNAMICS OF PBF MOLECULES

EXPENSES BUDGET SUMMARY

	EXPENSES		EXPENSES		EXPENSES		PRE-ENCUMB	ENCUMBRANCE	BALANCE
		ACCOUNT	BUDGET	CURRENT MONTH	YEAR-TO-DATE	INCEPT-TO-DATE			
PL DEPT SUMMER FAC OTHER	631105	29,663.00	0.00	0.00	0.00	23,951.20	0.00	0.00	5,711.80
PL GRAD RESEARCH ASST	632505	88,284.00	0.00	0.00	5,212.05	63,078.04	0.00	0.00	25,205.96
PL ACADEMIC OTHER	637005	5,125.00	0.00	0.00	0.00	16,377.50	0.00	0.00	-11,252.50
APPLIED BENEFITS	699905	15,375.00	0.00	0.00	166.79	11,883.02	0.00	0.00	3,491.98
STAFF WAGES	700005	0.00	0.00	0.00	0.00	830.40	0.00	0.00	-830.40
SUPPLIES & MATERIALS	740005	36,900.00	0.00	0.00	0.00	43,850.32	0.00	0.00	-6,950.32
EQUIPMENT	800005	107,917.00	0.00	0.00	0.00	121,390.73	0.00	0.00	-13,473.73
EQUIP-FABRICATED/ASSEMBLED	802505	0.00	936.32	0.00	9,498.71	16,619.93	0.00	0.00	-16,619.93
DOMESTIC TRAVEL	821005	37,197.00	0.00	0.00	1,856.20	21,781.49	0.00	0.00	15,415.51
FOREIGN TRAVEL	822005	0.00	0.00	0.00	0.00	5,271.03	0.00	0.00	-5,271.03
PROFESSIONAL SERVICES	872005	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TECHNICAL MEETING EXPENSE	875505	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CONT & RELATED CURRENT EXP	880005	0.00	0.00	0.00	0.00	6,520.80	0.00	0.00	-6,520.80
TUITION RATE	932105	11,477.00	0.00	0.00	833.93	9,503.50	0.00	0.00	1,973.50
OVERHEAD	960005	102,021.00	0.00	0.00	3,472.82	92,901.04	0.00	0.00	9,119.96
TOTAL EXPENSES		433,959.00	936.32		21,040.50	433,959.00	0.00	0.00	0.00

Posted 04-08-11

BA

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Report ID: OUGL0006
 Bus Unit: NORMN--
 Fiscal Year 2011 Period 9
 Currency USD

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 UNIVERSITY OF OKLAHOMA
 DETAILED LISTING OF COMMITMENTS VS. BUDGET

Page No. 14
 Run Date 04/01/2011
 Run Time 09:51:44

ACCOUNT	DESCRIPTION	DATE	SRC	JRNL ID	REF	SUBID	LINE	BUDGET	PRE-ENCUMB	ENCUMBRANCE	EXPENSE	BALANCE
50070	DOE/ARGONNE											
105053400	DYNAMICS OF PBF MOLECULES											
632505	PL GRAD RESEARCH ASST							0.00	0.00	0.00	5,212.05	-5,212.05
632505	- Current Month							0.00	0.00	0.00	0.00	0.00
632505	- YTD Balance							0.00	0.00	0.00	5,212.05	-5,212.05
.99905	APPLIED BENEFITS							0.00	0.00	0.00	166.79	-166.79
699905	- Current Month							0.00	0.00	0.00	0.00	0.00
699905	- YTD Balance							0.00	0.00	0.00	166.79	-166.79
802505	EQUIP-FABRICATED/ASSEMBLED							0.00	0.00	0.00	8,562.39	-8,562.39
	FABRICATED EQUIPMENT INVOICES										844.87	
	ALLEN AVIONICS, INC										91.45	
802505	- Current Month							0.00	0.00	0.00	936.32	-936.32
802505	- YTD Balance							0.00	0.00	0.00	9,498.71	-9,498.71
821005	DOMESTIC TRAVEL							0.00	0.00	0.00	1,856.20	-1,856.20
821005	- Current Month							0.00	0.00	0.00	0.00	0.00
821005	- YTD Balance							0.00	0.00	0.00	1,856.20	-1,856.20
932105	TUITION RATE							0.00	0.00	0.00	833.93	-833.93
2105	- Current Month							0.00	0.00	0.00	0.00	0.00
932105	- YTD Balance							0.00	0.00	0.00	833.93	-833.93
960005	OVERHEAD							0.00	0.00	0.00	3,472.82	-3,472.82
960005	- Current Month							0.00	0.00	0.00	0.00	0.00
960005	- YTD Balance							0.00	0.00	0.00	3,472.82	-3,472.82
105053400	Department Total - Current Month							0.00	0.00	0.00	936.32	-936.32
105053400	Department Total - YTD							0.00	0.00	0.00	21,040.50	-21,040.50

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