Proposal for a Sensitive Search for the Electric Dipole Moment of the Electron with Matrix-Isolated Radicals

M. G. Kozlov
Petersburg Nuclear Physics Institute, Gatchina 188300, Russia

Andrei Derevianko
Department of Physics, University of Nevada, Reno, Nevada 89557, USA

(Received 16 February 2006; published 8 August 2006)

We propose using matrix-isolated paramagnetic diatomic molecules to search for the electric dipole moment of the electron (*e*EDM). As was suggested by Shapiro in 1968, the *e*EDM leads to a magnetization of a sample in the external electric field. In a typical condensed matter experiment, the effective field on the unpaired electron is of the same order of magnitude as the laboratory field, typically about 10^5 V/cm. We exploit the fact that the effective electric field inside heavy polar molecules is on the order of 10^{10} V/cm. This leads to a huge enhancement of the Shapiro effect. Statistical sensitivity of the proposed experiment may allow one to improve the current limit on *e*EDM by 3 orders of magnitude in a few hours accumulation time.

DOI: 10.1103/PhysRevLett.97.063001 PACS numbers: 32.80.Ys, 11.30.Er, 13.40.Em

The searches for the elusive electric dipole moment of the electron (*e*EDM) are motivated by the fact that the existence of a permanent EDM of a particle violates both parity (*P*) and time-reversal (*T*) symmetries. Because of the compelling arguments of the *CPT* theorem, the *T* violation implies *CP* violation, a subject of great interest in the physics of fundamental interactions [1]. The current experimental limit on *e*EDM [2] is close to the predictions of many extensions to the standard model of elementary particles, such as "naive" supersymmetry (SUSY) [3,4]. Other SUSY extensions yield *e*EDM a few orders of magnitude below the present limit. Here we propose an *e*EDM search that may constrain *e*EDM at that important level. Our proposal relies on the fact that the thermodynamically averaged *e*EDM (and thus the electron's magnetic moment aligned with *e*EDM) is oriented along the electric field. We propose to employ polarized molecular radicals frozen in a rare-gas matrix and measure the *e*EDM-induced magnetic field generated by the sample. Conservative estimates project that the present limit on *e*EDM can be improved by several orders of magnitude.

The present limit on *e*EDM,

$$|d_e| < 1.6 \times 10^{-27} e \cdot \text{cm}, \tag{1}$$

is derived from a high-precision measurement [2] with a beam of Tl atoms. In such experiments, one spectroscopically searches for a tiny *e*EDM-induced splitting of the magnetic sublevels of an atom in an externally applied electric field.

New atomic *e*EDM experiments plan to use optical trapping [5]. There are two other major trends aimed at improving the experimental sensitivity to *e*EDM: (i) employing molecules instead of atoms in spectroscopic experiments [6–8] and (ii) nonspectroscopic solid-state experiments [9–11]. Here we propose to merge these two trends by searching for *e*EDM with molecules trapped in a cold matrix of rare-gas atoms (see Fig. 1). We argue that this scheme combines advantages of both techniques. Indeed, the *e*EDM effects in molecules are markedly amplified because of the strong internal molecular electric field [12], much larger than attainable laboratory fields. In the present solid-state schemes, the atomic enhancement of the external electric field for ions of a solid is of the order of unity [10]. By using matrix-isolated diatomic radicals, one can gain up to 6 orders of magnitude in the effective electric field. At the same time, one retains a great statistical sensitivity of the solid-state searches. We show that this particular combination seems to drastically improve sensitivity of the *e*EDM search.

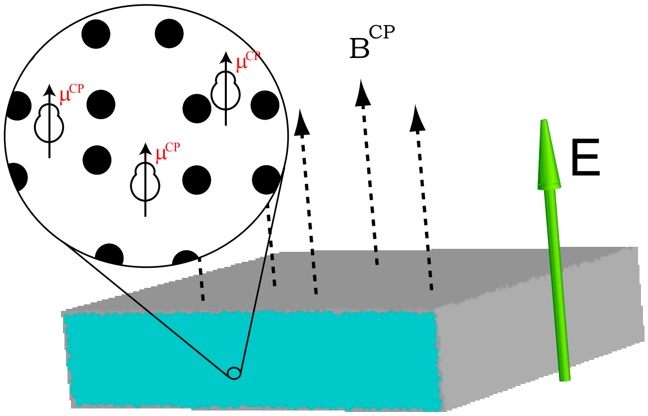

FIG. 1 (color online). Scheme of searching for EDM of an electron with diatomic radicals embedded in a matrix of rare-gas atoms. A polarizing electric field *E* is applied to the matrix. As a result, molecular *CP*-violating magnetic moments μ^{CP} become oriented and generate ultraweak magnetic field B^{CP}. By measuring B^{CP}, one places constraints on *e*EDM.

Let us review important aspects of the nonspectroscopic solid-state search for the *e*EDM. Introduced by Shapiro [13], this scheme exploits the link between EDM of the electron and its spin $\boldsymbol{d} = d_e \boldsymbol{\sigma}$ and, therefore, its magnetic moment $\boldsymbol{\mu}_e \approx -\mu_B \boldsymbol{\sigma} = -\mu_B \boldsymbol{d}/d_e$. In an external E field, because of the coupling of the *e*EDM to the E field, thermal populations of the spin-up and spin-down states slightly differ, leading to the magnetization of the sample. By measuring the generated magnetic field, one derives constraints on the *e*EDM. A proof-of-concept experiment was carried out in 1978 by Vasiliev and Kolycheva [14]. At that time, the solid-state experiment appeared to be less sensitive to the *e*EDM than the spectroscopic beam experiments. It is only very recently that the advances in magnetometery (see [15], and references therein) have revived an interest in the solid-state *e*EDM searches [9,10,16,17]. Alternatively, one can look for a voltage induced in a sample in external magnetic field [11].

We focus on molecular radicals (i.e., molecules with unpaired spin) in the ground ${}^2\Sigma_{1/2}$ state. Consider a sample of radicals in thermodynamic equilibrium at temperature T. Because of the *e*EDM coupling to the internal molecular E field, spin substates in a molecule have slightly different energies. This mechanism leads to a thermodynamically averaged CP-violating (P, T-odd) magnetic moment per molecule $\langle \mu^{CP} \rangle \sim \mu_B d_e E_{\mathrm{eff}}/(k_B T)$, where E_{eff} is the large molecular effective electric field acting on the EDM of the unpaired electron. E_{eff} grows $\propto Z^3$ with the nuclear charge Z of the heavier molecular constituent [18,19], and one would choose to work with heavy radicals. Such molecules as BaF, YbF, HgF, and HgH belong to this broad category. We found that mercury hydride (HgH) has parameters most suitable for the proposed search; see Table I. For the HgH molecule $E_{\mathrm{eff}} \approx 8 \times 10^{10}$ V/cm [25], and its ESR spectrum in Ar matrix has been studied in Ref. [26].

TABLE I. Parameters of several heavy molecules with the ground state ${}^2\Sigma_{1/2}$. Molecular dipole moments D were measured in Refs. [20–22]. Polarization $\langle n_z \rangle$, the maximal number density $n_{\max}$, and the accumulation time t_{acc} required to reach $S/N = 1$ for the current limit on *e*EDM (1). These parameters are calculated with the help of Eqs. (4), (7), and (12), for $E = 10$ kV/cm, $T = 1$ K, and sample volume 0.1 cm^3.

Molecule	E_{eff} [a] (10^9 V/cm)	D (D)	$\langle n_z \rangle$	$n_{\max}$ (10^{20} cm^{-3})	t_{acc} (ms)
BaF	8	3.17	0.13	0.03	300
YbF	26	3.91	0.16	0.02	30
HgH	79	0.47	0.02	1.5	3

[a] The effective electric field for BaF and YbF was calculated in Refs. [23,24]. For HgH, we rescale results from Ref. [25].

For diatomics, the moment $\langle \mu^{CP} \rangle$ is directed along the molecular axis. For a randomly oriented sample, however, the net magnetization would vanish. When an external E field is applied, it couples to the traditional molecular electric dipole moment D and orients the molecules. Taking into account molecular polarization, the CP moment can be expressed as

$$\langle \mu^{CP}_{\mathrm{mol}} \rangle \approx \mu_B \frac{d_e E_{\mathrm{eff}}}{k_B T} \times \langle n_z \rangle, \tag{2}$$

where $\langle n_z \rangle$ is the average projection of the molecular axis onto the E field (the field is directed along the z axis). Now the sample acquires a macroscopic magnetization. This magnetization generates an ultraweak magnetic field B^{CP} proportional to *e*EDM

$$B^{CP} = 4\pi \gamma n \langle \mu^{CP}_{\mathrm{mol}} \rangle, \tag{3}$$

where n is the molecular number density and γ is a geometry-dependent factor. For example, near the center of a disk-shaped sample of radius R and thickness L, $\gamma = L/2R$.

Orientation of the B field (3) is linked to that of the applied E field through $\langle n_z \rangle$. Such a link is forbidden in traditional electrodynamics. Its very presence is a manifestation of the parity and time-reversal violation. By measuring B^{CP}, one constrains *e*EDM via Eqs. (2) and (3). It is apparent that maximizing n is beneficial. However, bringing radicals together is problematic—they react chemically. Here is where the matrix isolation technique [27] becomes key. In this well-established method, the molecules are co-deposited with rare-gas atoms or other species onto a cold ($T \sim 1$ K) substrate and become trapped in the matrix. Small trapped molecules exhibit properties similar to those for free molecules, and a variety of studies, including determination of hyperfine-structure constants, have been carried out.

There is an upper limit on the density of trapped molecules; to avoid spin alignment in the subsystem of guest molecules, one requires that thermal agitations are stronger than dipole-dipole interactions between the molecules. We can estimate the maximum density as:

$$n_{\max} \approx \frac{3}{4\pi} \frac{k_B T}{D^2}. \tag{4}$$

A particular advantage of HgH is that its dipole moment is relatively small, $D = 0.47$ Debye [22] and at $T = 1$ K, the density $n_{\max} \approx 1.5 \times 10^{20}$ cm^{-3}.

Estimate (4) agrees with experimental observations that a 1:100 guest to host ratio is possible. According to Ref. [28], the realistic matrix thickness and area are $L = 1$ mm and $S = 1$ cm^2. That corresponds to $\gamma \approx 0.1$ in (3). A recently developed low density plasma beam source [29] produces a permanent beam of heavy radicals with intensity $\sim 10^{18}$ mol/sterad/s. Placing a 1 cm^2 target at 20 cm from the source, one can accumulate necessary number of radicals, i.e., 10^{19}, in 1 h.

How are the relevant molecular properties modified by the matrix environment? A free nonrotating molecule may be described by the electronic wave function $|\Omega\rangle$, with

$\Omega = \pm 1/2$ characterizing projection of spin onto molecular axis. The time-reversal operation T converts Ω states into each other: $|\Omega\rangle \xrightarrow{T} |-\Omega\rangle$. In the matrix, a molecule can be considered as an individual entity perturbed by the host atoms. The local symmetry of the perturbing fields depends on the position of the molecule in the matrix. Independent of the spatial symmetry, the time-reversal symmetry remains. According to Kramers' theorem, in the absence of magnetic fields, all levels of diatomics with half-integer spin remain twofold degenerate for any possible electric field.

EDM interaction operates at short distances near the heavier nucleus. Expanding the electronic wave function in partial waves, we notice that contributions to the eEDM signal of total angular momenta beyond $s_{1/2}$ and $p_{1/2}$ waves are strongly suppressed because of the growing centrifugal barrier and properties of the eEDM [30]. The truncated wave function has the $C_{\infty,v}$ symmetry, and Ω still remains a good quantum number for the degenerate states of matrix-isolated radicals. Within this approximation, the effective molecular Hamiltonian in the external field E reads

$$H_{\rm eff} = -\boldsymbol{D} \cdot \boldsymbol{E}^* + 2d_e E_{\rm eff}\Omega, \tag{5}$$

where E^* is the microscopic E field; for small fields, $E^* = E/\varepsilon$. We used $H_{\rm eff}$ to arrive at Eq. (2).

Using the estimate (2) with the present limit on eEDM (1), we obtain for the thermally induced CP-odd magnetic moment of HgH molecule trapped at $T = 1$ K

$$\langle \mu^{CP}_{\rm mol}({\rm HgH})\rangle < 1.4 \times 10^{-12}\langle n_z\rangle \mu_B. \tag{6}$$

It is instructive to compare this value to the *permanent* molecular CP-violating magnetic moment introduced by us in Ref. [17]. This moment arises due to a magnetization of the molecule by its own electric field (irrespective of the temperature). The largest μ^{CP} for diamagnetic molecules was found for BiF, for which $\mu^{CP} < 3 \times 10^{-17}\langle n_z\rangle\mu_B$, much smaller than the *thermally induced* CP-odd moment (6). Therefore, here we may neglect the *permanent* μ^{CP}.

An important parameter entering $\langle \mu^{CP}_{\rm mol}\rangle$ is the degree of molecular polarization $\langle n_z\rangle$ in the external E field. Free diatomic molecules can be easily polarized by the laboratory fields $\sim 10^4$ V/cm, but there is a paucity of data on polarizing matrix-isolated molecules [31]. Certainly, the rotational dynamics of the guest molecule is strongly affected by the matrix cage. The molecular axis evolves in a complex multivalley potential, subject to the symmetry imposed on the molecules by the matrix cage. Depending on the barrier height between different spatially oriented valleys, the guest molecule may execute either hindered rotation or librations about the valley minima. Reference [32] reports evidence for hindered rotation of HXeBr, and Ref. [33] suggests that other hydrides can rotate. Note also that for the Ar matrix the cell size is 4.5 Å, while the internuclear distance for HgH is only 1.7 Å. That gives us confidence that the HgH radical can be polarized by the external electric field.

We will distinguish between two limiting cases of molecular polarization: strong and weak fields. In the former limit $\langle n_z\rangle \sim 1$, and in the latter,

$$\langle n_z\rangle = \frac{1}{Z}\sum_{n_z} n_z \exp\left(\frac{DE^* n_z}{k_B T}\right) \approx \frac{DE^*}{k_B T}\langle n_z^2\rangle. \tag{7}$$

For isotropic orientational distribution, characteristic for the polycrystalline matrices, $\langle n_z^2\rangle = 1/3$, and we get

$$\langle \mu^{CP}_{\rm mol}\rangle \approx \frac{1}{3}\mu_B \frac{DE^*}{k_B T}\frac{E_{\rm eff} d_e}{k_B T}. \tag{8}$$

The dielectric constant of the rare-gas matrix is close to unity, but addition of polar molecules results in

$$\varepsilon \approx 1 + 4\pi n\alpha = 1 + 4\pi n \frac{D^2\langle n_z^2\rangle}{k_B T} \approx 1 + \frac{4\pi}{3} n \frac{D^2}{k_B T}, \tag{9}$$

where α is molecular polarizability. For maximum density (4), $\varepsilon \approx 2$ and $E^* \approx E/2$.

The parameter differentiating the weak- and the high-field regimes is the ratio $DE^*/k_B T$. For HgH trapped at $T = 1$ K, the transition occurs at $E^* \approx 100$ kV/cm. The breakdown fields for the rare-gas matrices are unknown; we only notice that for liquid Xe it is 400 kV/cm so that both weak- and high-field regimes may be possibly realized. The moderate $E = 10$ kV/cm field corresponds to $\langle n_z\rangle \approx 0.02$.

Finally, we proceed to evaluating the sensitivity of the proposed eEDM search. There are two crucial criteria to consider: weakest measurable B field and signal-to-noise ratio. Presently, the most sensitive measurement of magnetic fields has been carried out by the Princeton group (see [15], and references therein). This group has reached the sensitivity level of 5.4×10^{-12} G/$\sqrt{\rm Hz}$. A projected experimental sensitivity of 3×10^{-15} G/$\sqrt{\rm Hz}$ is published in Ref. [9]. We find that for $\langle n_z\rangle \sim 1$ and for $\gamma = 0.1$ the present eEDM limit may be recovered within an integration time of $t = 5$ s for the demonstrated sensitivity and within 10^{-6} s for the projected sensitivity. Alternatively, during a week-long measurement, the present eEDM limit may be improved by 3×10^2 for the demonstrated and by 6×10^5 for the projected B-field sensitivity. These values are reduced by a factor of 50 for a moderate 10 kV/cm polarizing field.

In addition to limitations imposed by the weakest measurable B field, one must also consider signal-to-noise ratio [34]. As we pointed out above, the thermally induced $\langle \mu^{CP}_{\rm mol}\rangle$ of radicals is many orders larger than permanent $\mu^{CP}_{\rm mol}$ of diamagnetic molecules discussed in Ref. [17]. The magnetic noise from paramagnetic radicals is also much higher as they have traditional magnetic moments associated with unpaired electron spin,

$$\langle\mu_{\mathrm{mol}}\rangle = 2\mu_B\Omega\langle n_z\rangle. \tag{10}$$

These moments lead to random magnetization of the sample and generate a fluctuating B field. Unlike B^{CP}, this field is not correlated with the direction of the external E field, and it is the main source of the noise. In our case, the signal-to-noise ratio is

$$S/N = 3\frac{\langle\mu_{\mathrm{mol}}^{CP}\rangle}{\mu_B}\sqrt{\mathcal{N}\frac{t}{\tau}}, \tag{11}$$

where $\mathcal{N}$ is the number of molecules, t is the observation time, and τ is the correlation time for the random thermal magnetization. Factor 3 at the right-hand side appears because of the averaging of the magnetic moment (10) over orientations of the molecular axis $\boldsymbol{n}$.

For a strong spin-rotation coupling, as in the case of HgH, τ is determined by interaction of molecular axis with environment. One such mechanism is the dipolar interaction between guest radicals, so that $\tau \sim \hbar/(D^2n) = 4\pi\hbar/(3k_BT)$ for the optimal density (4). For the weak-field limit (8), we get the final expression for S/N:

$$S/N = \frac{3}{8\pi}\frac{EE_{\mathrm{eff}}d_e}{k_BT}\sqrt{Vt/\hbar}, \tag{12}$$

where V is the sample volume. This equation is used in Table I to estimate the accumulation time needed to reproduce the current limit (1). For the HgH molecule, we find that, for a volume of 0.1 cm^3 and strong polarizing field, the present eEDM limit may be recovered within $t = 10^{-6}$ s (3 ms for the field 10 kV/cm). By integrating the signal for one week, the present eEDM limit may be improved by a factor of 2×10^6. Note that these estimates are close to the estimates based on the projected sensitivity to the weak magnetic fields [9].

To summarize, our proposed eEDM search combines advantages of the strong intermolecular field with a high attainable number density of molecules embedded in a matrix of rare-gas atoms. We argue that our proposal has the potential of improving the present eEDM limit by several orders of magnitude. That will allow constraining the "new physics" beyond the standard model at an important new level and, in particular, testing predictions of competing SUSY models.

We thank D. Budker, T. Isaev, L. Knight, S. Lamoreaux, S. Porsev, M. Romalis, V. Ryabov, I. Savukov, R. Sheridan, O. Sushkov, and I. Tupitsyn for valuable comments and discussions. This work is supported by the Russian Foundation for Basic Research, Grant No. 05-02-16914, by NSF, and by NIST.

---

[1] I. I. Bigi and A. I. Sanda, *CP Violation* (Cambridge University Press, Cambridge, England, 2000).

[2] B. C. Regan, E. D. Commins, C. J. Schmidt, and D. DeMille, Phys. Rev. Lett. **88**, 071805 (2002).

[3] E. N. Fortson, P. Sandars, and S. Barr, Phys. Today **56**, No. 6, 33 (2003).

[4] K. P. Jungmann, Nucl. Phys. **A751**, 87 (2005).

[5] C. Chin, V. Leiber, V. Vuletic, A. J. Kerman, and S. Chu, Phys. Rev. A **63**, 033401 (2001).

[6] J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. **89**, 023003 (2002).

[7] J. J. Hudson *et al.*, physics/0509169.

[8] D. DeMille *et al.*, Phys. Rev. A **61**, 052507 (2000).

[9] S. K. Lamoreaux, Phys. Rev. A **66**, 022109 (2002).

[10] T. N. Mukhamedjanov, V. A. Dzuba, and O. P. Sushkov, Phys. Rev. A **68**, 042103 (2003).

[11] B. J. Heidenreich *et al.*, Phys. Rev. Lett. **95**, 253004 (2005).

[12] O. P. Sushkov and V. V. Flambaum, Sov. Phys. JETP **48**, 608 (1978).

[13] F. L. Shapiro, Sov. Phys. Usp. **11**, 345 (1968).

[14] B. V. Vasiliev and E. V. Kolycheva, Sov. Phys. JETP **47**, 243 (1978).

[15] I. K. Kominis, T. W. Kornack, J. C. Allred, and M. V. Romalis, Nature (London) **422**, 596 (2003).

[16] V. G. Baryshevsky, Phys. Rev. Lett. **93**, 043003 (2004).

[17] A. Derevianko and M. G. Kozlov, Phys. Rev. A **72**, 040101(R) (2005).

[18] V. V. Flambaum, Yad. Fiz. **24**, 383 (1976) [Sov. J. Nucl. Phys. **24**, 199 (1976)].

[19] P. G. H. Sandars, Phys. Lett. **14**, 194 (1965).

[20] W. E. Ernst, J. Kandler, and T. Torring, J. Chem. Phys. **84**, 4769 (1986).

[21] B. E. Sauer, J. Wang, and E. A. Hinds, Phys. Rev. Lett. **74**, 1554 (1995).

[22] O. Nedelec, B. Majournat, and J. Dufayard, Chem. Phys. **134**, 137 (1989).

[23] M. Kozlov and L. Labzowski, J. Phys. B **28**, 1933 (1995).

[24] M. G. Kozlov, J. Phys. B **30**, L607 (1997).

[25] M. G. Kozlov, Sov. Phys. JETP **62**, 1114 (1985).

[26] A. C. Stowe and L. B. Knight, Jr., Mol. Phys. **100**, 353 (2002).

[27] *Chemistry and Physics of Matrix-Isolated Species*, edited by L. Andrews and M. Moskovits (Elsevier Science, New York, 1989).

[28] L. B. Knight, Jr. and R. Sheridan (private communication).

[29] V. L. Ryabov, V. F. Ezhov, and M. A. Kartasheva, Pis'ma Zh. Tekh. Fiz. **32**, 26 (2006).

[30] I. B. Khriplovich and S. K. Lamoreaux, *CP Violation without Strangeness* (Springer, Berlin, 1997).

[31] T. Kiljunen, B. Schmidt, and N. Schwentner, Phys. Rev. Lett. **94**, 123003 (2005).

[32] L. Khriachtchev *et al.*, J. Chem. Phys. **122**, 014510 (2005).

[33] W. Weltner, Jr., *Magnetic Atoms and Molecules (Dover Books on Physics and Chemistry)* (Dover, New York, 1990).

[34] D. Budker, S. K. Lamoreaux, A. O. Sushkov, and O. P. Sushkov, Phys. Rev. A **73**, 022107 (2006).