

Hyperfine and Zeeman interactions of the $a(1)[^3\Sigma_1^+]$ state of PbO

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The role of the interaction with the nearest electronic state $^3\Sigma_{0-}^+$ on the hyperfine structure and magnetic properties of the $a(1)[^3\Sigma_1^+]$ state of PbO is assessed. The accounting for this contribution leads to difference between g -factors of the $J = 1$ Ω -doublet levels, $\Delta g = 37 \times 10^{-4}$, that is in a good agreement with the experimental datum $\Delta g = 30(8) \times 10^{-4}$. The contribution of this interaction rapidly grows with J . For $J = 30$ the difference of g -factors of Ω -doublet states reaches 100%; for hyperfine constants it is 18%. These differences also depend on the electric field and for $E = 11$ V/cm for ^{207}PbO the difference in g -factors turn to zero. The latter is important for suppressing systematic effects in the electron electric dipole moment search experiment.

The use of $a(1)$ excited state of PbO molecule has been proposed to search for electric dipole moment (EDM) of the electron [1]. This experiment is a serious test of the “new physics” beyond the Standard Model including different supersymmetric models [2–5]. Because of that the molecule was intensively investigated both theoretically [6–10] and experimentally [11–13].

In the adiabatic approximation rotational levels of the $a(1)$ state of PbO are determined by the effective spin-rotational Hamiltonian

$$H_{sr} = B' \mathbf{J}^2 + A_{\parallel} (\mathbf{J}^e \cdot \mathbf{n})(\mathbf{I} \cdot \mathbf{n}) + \mu_B G_{\parallel} (\mathbf{J}^e \cdot \mathbf{n})(\mathbf{B} \cdot \mathbf{n}) - D \mathbf{n} \cdot \mathbf{E} \quad (1)$$

Here B' is the rotational constant, \mathbf{J} , \mathbf{J}^e , \mathbf{I} are the electron-rotational, electron and nuclear angular momentum operators, respectively (in this paper we will measure angular momentum in units of \hbar), \mathbf{E} and \mathbf{B} are external electric and magnetic fields, D is the molecular-frame dipole moment, \mathbf{n} is a unit vector along the molecular axis, ζ , directed from Pb to O, μ_B is Bohr magneton. The hyperfine constant A_{\parallel} and g -factor G_{\parallel} are determined by the expressions [14]

$$A_{\parallel} = \frac{1}{\Omega} \frac{\mu_{\text{Pb}}}{I} \langle \Psi_{3\Sigma_{\pm 1}^+}^e | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \mathbf{r}_i}{r_i^3} \right)_{\zeta} | \Psi_{3\Sigma_{\pm 1}^+}^e \rangle, \quad (2)$$

$$G_{\parallel} = \frac{1}{\Omega} \langle \Psi_{3\Sigma_{\pm 1}^+}^e | J_{\zeta}^e + S_{\zeta}^e | \Psi_{3\Sigma_{\pm 1}^+}^e \rangle, \quad (3)$$

where \mathbf{S}^e is the electron spin operator, μ_{Pb} is the magnetic moment of ^{207}Pb , $\boldsymbol{\alpha}_i$ are the Dirac matrices for the i -th electron, \mathbf{r}_i is its radius-vector in the coordinate system centered on the Pb atom, $\Omega = \langle \Psi_{3\Sigma_{\pm 1}^+}^e | J_{\zeta}^e | \Psi_{3\Sigma_{\pm 1}^+}^e \rangle = \pm 1$. From naturally abundant isotopes only ^{207}Pb ($I = 1/2$) has nonzero μ_{Pb} , for ^{208}Pb and ^{206}Pb $I = 0$ and, therefore, $\mu_{\text{Pb}} = 0$.

The parameters B' , A_{\parallel} , G_{\parallel} and D can be obtained both theoretically from calculation of the *electronic* wavefunction $\Psi_{a(1)}^e$ and by fitting the experimentally observed

transitions to the parameters of the spin-rotational Hamiltonian (1). Comparison of theoretical and experimental values gives us information about accuracy of the calculated wavefunction $\Psi_{a(1)}^e$ and, therefore, also gives information about accuracy of the calculated effective electric field, W_d , seen by an unpaired electron [7, 8]. Note, that W_d can not be measured independently, but it is required for extracting d_e from the EDM experiment. The experimentally observed parameters A_{\parallel} , G_{\parallel} also can be used for a semiempirical evaluation of W_d [6].

Previous investigations of PbO were based on the spin-rotational Hamiltonian (1). The main goal of the present work is to account for the interaction with the nearest electronic state $^3\Sigma_{0-}^+$, which modifies the form of this Hamiltonian. To the best of our knowledge this is the first investigation of such kind for open shell diatomics.

In the present paper the hyperfine structure of rotational levels was obtained by numerical diagonalization of the Hamiltonian in the basis set of electronic rotational wavefunctions

$$\Psi_{3\Sigma_{\pm 1}^+}^e \theta_{M, \pm 1}^J(\alpha, \beta) U_{M_I}, \Psi_{3\Sigma_{0-}^+}^e \theta_{M, 0}^J(\alpha, \beta) U_{M_I}, \quad (4)$$

where $\theta_{M, \Omega}^J(\alpha, \beta) = \sqrt{(2J+1)/4\pi} D_{M, \Omega}^J(\alpha, \beta, \gamma = 0)$ and U_{M_I} are rotational and nuclear spin wavefunctions, M and $M_I = \pm 1/2$ are projections of the angular momenta, \mathbf{J} and \mathbf{I} , on the laboratory axis z . When *electronic* matrix elements are known then matrix elements on the basis set (4) can be calculated with the help of the angular momentum algebra [15]. Required diagonal *electronic* matrix elements, being, in fact, the parameters of the spin-rotational Hamiltonian (1), are known from experiments. For the fifth vibrational level of the $a(1)$ state of PbO they are $B' = 0.235296$ cm $^{-1}$, $A_{\parallel} = -4.1$ GHz, $G_{\parallel} = 1.857$, $D = 1.28$ a.u. [11–13]. For purposes of the present study, it is not required to account for the small difference between the rotational constants of $^{206, 207, 208}\text{PbO}$ molecules. The differences in properties discussed below are relevant only to the fact that the isotope ^{207}Pb has hyperfine structure. The off-diagonal *electronic* matrix elements were calculated in the present study by the configuration interaction method with the

generalized relativistic effective core potential [16, 17]. The scheme of the calculation is the same as that in the paper [8]. The calculated matrix elements are

$$\frac{\Delta}{2} = B' \langle \Psi_{3\Sigma_1^+}^e | J_+^e | \Psi_{3\Sigma_0^+}^e \rangle = 0.17 \text{ cm}^{-1}, \quad (5)$$

$$\frac{\mu_{\text{Pb}}}{I} \langle \Psi_{3\Sigma_1^+}^e | \sum_i \left(\frac{\boldsymbol{\alpha}_i \times \mathbf{r}_i}{r_i^3} \right)_+ | \Psi_{3\Sigma_0^+}^e \rangle = -0.7 \text{ GHz}, \quad (6)$$

$$G_{\perp} = \langle \Psi_{3\Sigma_1^+}^e | J_+^e + S_+^e | \Psi_{3\Sigma_0^+}^e \rangle = 1.5. \quad (7)$$

It is known that Hamiltonian (1) leads to two-fold degeneracy of levels with different signs of Ω . This degeneracy is in fact only approximate. When the interaction (5) is taken into account each rotational level splits into two sublevels, called Ω -doublet levels. One of them is even ($p = 1$) and the other one is odd ($p = -1$) with respect to changing the sign of electrons and nuclear coordinates. In order to reproduce experimental value of the Ω -doubling, $5.6J(J+1)$ MHz [12], the matrix element (5) has to be equal to 0.15 cm^{-1} . We consider this a good agreement, but will use experimental value hereafter. The states with $p = (-1)^J$ are denoted as e and with $p = (-1)^{J+1}$ as f states. Note that the wavefunctions $\Psi_{3\Sigma_0^+}^e \theta_{M,0}^J(\alpha, \beta) U_{M_I}$ are f states, and they do not interact (see below) with e states of the $a(1)$, unless parity is not conserved, due to weak interactions.

Interactions (6) and (7) lead to different hyperfine structure and magnetic properties of the e and f levels. One can estimate from the second order perturbation theory that contribution from the terms

$$\begin{aligned} & |\langle \Psi_{3\Sigma_{\pm 1}^e} \theta_{M,\pm 1}^J U_{M_I} | \hat{H}_{\text{hfs(mag)}} | \Psi_{3\Sigma_{0-}^e} \theta_{M,0}^J U_{M_I} \rangle|^2 \\ & / \left(E_{3\Sigma_1^+} - E_{3\Sigma_0^+} \right) \end{aligned} \quad (8)$$

is small. Here \hat{H}_{hfs} and \hat{H}_{mag} are Hamiltonians of the hyperfine interaction and the interaction with the external magnetic field, respectively. However, the terms

$$\begin{aligned} & 2\text{Re}(\langle \Psi_{3\Sigma_{\pm 1}^e} \theta_{M,\pm 1}^J U_{M_I} | 2B' \mathbf{J} \mathbf{J}^e | \Psi_{3\Sigma_{0-}^e} \theta_{M,0}^J U_{M_I} \rangle \times \\ & \langle \Psi_{3\Sigma_{0-}^e} \theta_{M,0}^J U_{M_I} | \hat{H}_{\text{hfs(mag)}} | \Psi_{3\Sigma_{\pm 1}^e} \theta_{M,\pm 1}^J U_{M_I} \rangle) \\ & / \left(E_{3\Sigma_1^+} - E_{3\Sigma_0^+} \right) \end{aligned} \quad (9)$$

are much larger and their influence on the spectrum of the $a(1)$ state is observable.

In Table I we give calculated g -factors for f states with different quantum numbers J of $^{206,208}\text{PbO}$ molecule. For e states calculated $g_e = 1.85700$ and is independent on J . We define g -factors so that the Zeeman splitting

TABLE I: The g -factors for f -states of $^{206,208}\text{PbO}$ as a function of J . For e states $g_e = 1.85700$ and is independent on J .

J	g_f	J	g_f
1	1.86074	10	2.06255
2	1.86822	12	2.14848
3	1.87943	15	2.30537
4	1.89438	20	2.64142
6	1.93549	25	3.07055
8	1.99155	30	3.59256

TABLE II: Calculated values of HFS as a function of J for f - and e -levels of ^{207}PbO . Results of Ref.[11] are given in the last column (see Eqs.(1) and (2) therein). These results are for both f - and e -levels.

J	this work		Ref. [11]
	f	e	
1	3188	3187	3195
2	1905	1903	1913
3	1356	1353	1358
5	863	858	859
10	458	449	449
15	317	304	304
20	248	230	230
30	181	154	154

is equal to $g_{e(f)} \mu_B B_z M / J(J+1)$. Our calculations were done using the finite field method.

The obtained difference $g_f - g_e = 37 \times 10^{-4}$ for $J = 1$ is in good agreement with the experimental result $g_f - g_e = 30(8) \times 10^{-4}$ [12]. As it is seen from Table I the difference is rapidly increasing with J , and for $J = 30$ g_f is about two times larger than g_e . Another point to note is that matrix elements (5) and (7) do not contribute to g_e and it remains J -independent and unchanged. This is due to the mentioned above parity selection rule. Limiting by the terms (9) we obtain

$$g_f - g_e = \frac{\Delta \cdot G_{\perp} \cdot J(J+1)}{\left(E_{3\Sigma_1^+} - E_{3\Sigma_0^+} \right)} = 1.87032 \times 10^{-3} J(J+1)$$

that is in a good agreement with Table I.

In Table II, the hyperfine splitting (HFS) calculated between $F = J - 1/2$ and $F = J + 1/2$ levels as a function of J is given for e and f states of ^{207}PbO . Also the results obtained by applying Eq. (1) and (2) of ref. [11] are listed. Eqs. (1) and (2) of ref. [11] give HFS in the framework of the Hamiltonian (1). The interaction with the $^3\Sigma_{0-}^+$ is not taken into account in the (1), therefore Eqs. (1) and (2) of ref. [11] give the same HFS for e and f states of the $a(1)$. Similarly to g factors, the hyperfine structure of e states is not affected when interactions (5) and (6) are taken into account. However, there is a small difference between the hyperfine splittings calculated by Eqs. (1) and (2) in Ref. [11] and that calculated for e states in this paper. This difference is related with the fact that the mixing between the states with $\Delta J = \pm 1$

in Eqs. (1) and (2) of Ref. [11] is taken into account in the framework of the second order perturbation theory, whereas in the current work it is calculated more accurately, by using the numerical diagonalization of the Hamiltonian.

In the electron EDM search experiment the Stark splitting between $J = 1, M \pm 1$ states of the e or f levels is measured. This Stark effect induced by the interaction with the electron EDM that violate both parity (P) and time reversal (T) invariance, and is not related with the (large) dipole moment D presented in the (1). For details see pp. 1–3 in Ref. [3]. In the external electric field the states $J = 1, M = \pm 1$ remain degenerate, unless both P and T are violated. However an external magnetic field remove degeneracy between them and can mimic the existence of the EDM. For $J = 1$ levels the systematics due to spurious magnetic fields can be suppressed if the difference between g_e and g_f can be made smaller [12]. The external electric field mixes e and f levels. Therefore, on the first glance, one can expect that when increasing the electric field the initial small difference between g_e and g_f can be made zero. However, it was found in [12] that this difference for $^{206,208}\text{PbO}$ is actually increases as the electric field increases. This fact was explained by M.G. Kozlov (see acknowledgments in [13]) by accounting for the mixing with $J = 2$ level. In the present paper we reproduce this result for spinless isotopes of lead and also calculate g -factors for $J = 1, F = 1/2, 3/2$ states of the ^{207}PbO . For ^{207}PbO , g -factors was defined so that the Zeeman shift is given by

$$g_{e(f)}\mu_B B_z \frac{F(F+1) + J(J+1) - 3/4}{2F(F+1)J(J+1)} M_F.$$

With this definition they will coincide with g -factors of $^{206,208}\text{PbO}$ in the limit of zero hyperfine interaction. The corresponding results are given in Fig. (1). One can see that difference between g_e and g_f for $J = 1, F = 3/2$ does not converge to zero as E increases. However, for $F = 1/2, J = 1$ at $E \approx 11$ V/cm g_e and g_f become equal. The plotted g_e and g_f for $J = 1$ $^{206,208}\text{PbO}$ are in agreement with Fig. (5) of ref. [13]. Large deviation of g -factors for $J = 1, F = 3/2$ of ^{207}PbO from those for $J = 1$ of $^{206,208}\text{PbO}$ is explained by mixing of the $J = 1, F = 3/2$ and $J = 2, F = 3/2$ levels of ^{207}PbO that is induced by the hyperfine interaction.

In the EDM experiment the maximum Stark splitting, $2W_d \cdot d_e$, between $F = 1/2, M_F = \pm 1/2$ levels is achieved for the fully polarized molecule. In Fig. (2) we plot the calculated Stark splitting between $F = 1/2, M_F = \pm 1/2$ levels as function of the external electric field. For $E = 11$ V/cm the obtained splitting is about 75% of the maximal value.

In this work we account for non-adiabatic interaction of $a(1)[^3\Sigma_1^+]$ state only with the state $^3\Sigma_{0-}^+$. There are several reasons for this. One can see [18, 19] that the $^3\Sigma_{0-}^+$ state is the nearest one to the $a(1)$ state. All other

states, except $^3\Delta$, are more than an order of magnitude further away. Accounting for the non-adiabatic interaction with the $^3\Delta_1$ state (the same $\Omega = 1$ as in $a(1)$) will lead only to a small modification of the parameters of the spin-rotational Hamiltonian (1). Since we use the experimental data, those interactions with the $^3\Delta_1$ and other $\Omega = 1$ states are taken into account. Though the interaction with $^3\Delta_2$ can not be described in the framework of the Hamiltonian (1), it will not lead in the leading order to the difference in properties of the f and e states that is a topic of this paper. Moreover, our calculation show that the corresponding matrix element

$$B' \langle \Psi_{^3\Sigma_1^+}^e | J_-^e | \Psi_{^3\Delta_2^+}^e \rangle \approx 3 \times 10^{-3} \text{ cm}^{-1}$$

is small as compared to (5). $\Omega = 3$ states are not mixed in the leading order due to the selection rule. The validity of the above approximation is approved by the fact that the calculated and the experimentally obtained differences of the g -factors for e and f $J = 1$ states are in good agreement.

Finally we have investigated the influence of the interaction with the nearest electronic state $^3\Sigma_{0-}^+$ on the hyperfine structure and magnetic properties of the $a(1)[^3\Sigma_1^+]$ state. We have shown that it is required for its accurate description, especially for g -factors. One can suppose that similar situation takes place also for other diatomics in $\Omega = 1$ states. It is found that the difference between g_e and g_f for ^{207}PbO is converged to zero at $E \approx 11$ V/cm. The latter is important for the suppressing systematic effects in the electron EDM search experiment.

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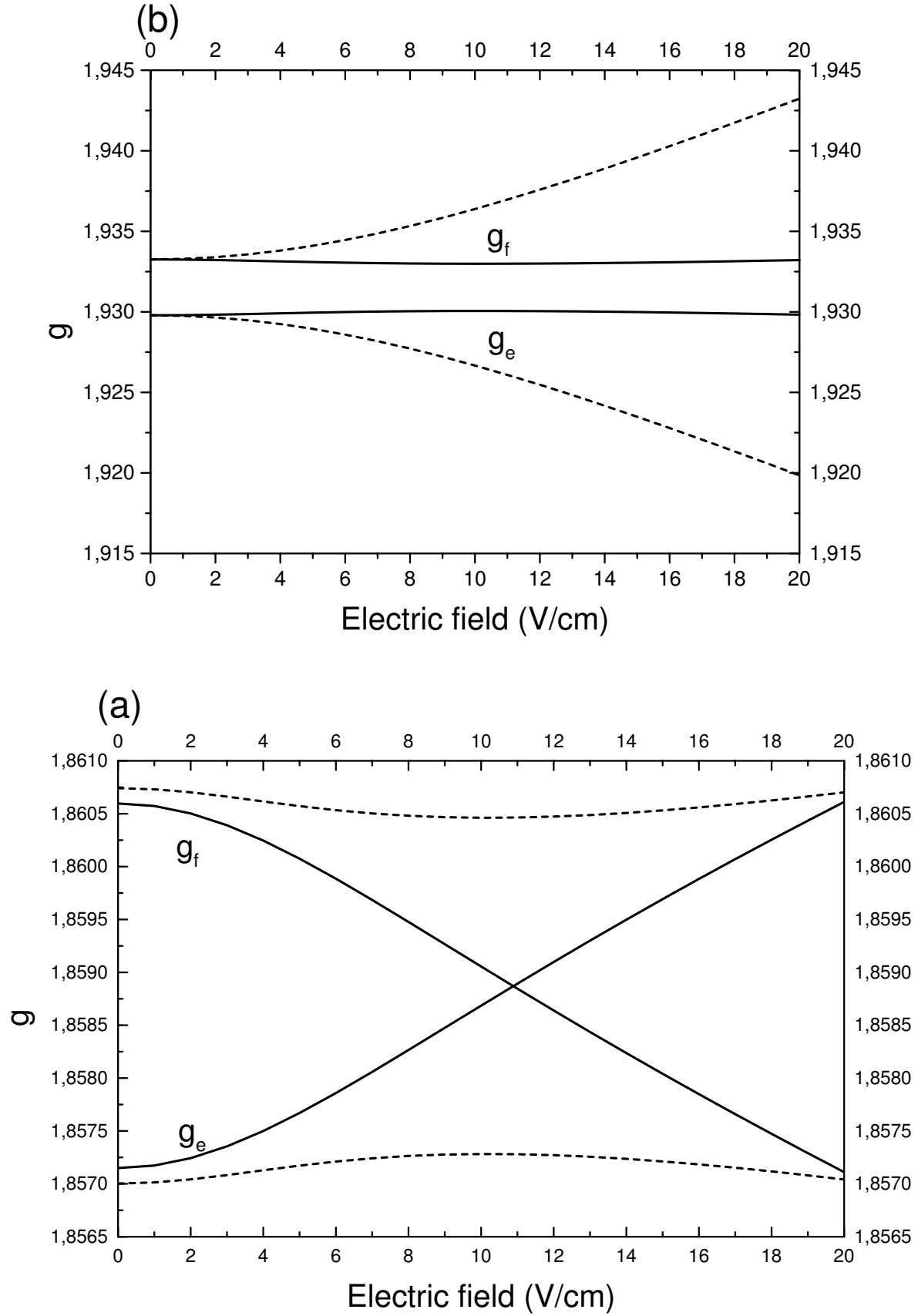


FIG. 1: Calculated g -factors for $e(g_e)$ and $f(g_f)$ states. (a) Solid lines correspond to $J = 1, F = 1/2$ hyperfine levels of ^{207}PbO , dashed lines correspond to $J = 1$ rotational levels of $^{206,208}\text{PbO}$. (b) Solid lines correspond to $J = 1, F = 3/2, |M_F| = 3/2$, dashed lines correspond to $J = 1, F = 3/2, |M_F| = 1/2$ hyperfine levels of ^{207}PbO

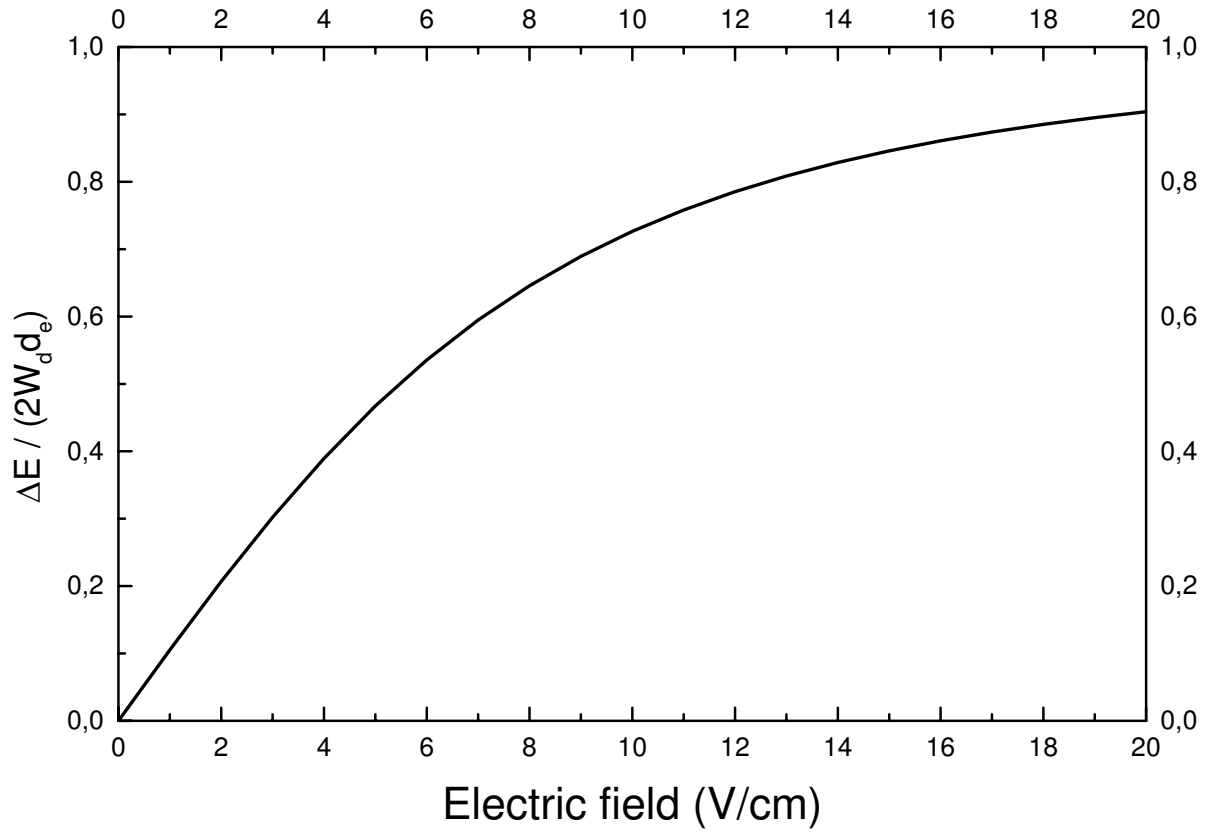


FIG. 2: EDM induced Stark splitting between $M_F = \pm 1/2$ levels of $J = 1, F = 1/2$ state of ^{207}PbO