Centrifugal correction to hyperfine structure constants in the ground state of lead monofluoride, PbF

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The sensitivity of the PbF molecule to the electron electric dipole moment has motivated detailed microwave spectroscopy. Previous theoretical approaches cannot fully explain the spectra. In turn, the explanation from “first principles” is very important both for molecular theory and for confirmation of the correctness of the interpretation of experimental data obtained with high precision. All of these issues are decisively addressed here. We have determined centrifugal correction parameters for hyperfine structure constants, both on lead and fluorine nuclei, of the $^2\Pi_{\pm 1/2}$ state of lead monofluoride. These parameters were obtained by fitting experimentally observed pure rotational transitions and from ab initio calculations. We show that taking this correction into account is required to reproduce the experimental transition energies obtained in [Phys. Rev. A 84, 022508 (2011)].

Interest in the theoretical study of PbF is motivated primarily by the proposed experiments to search for the simultaneous violation of time-reversal invariance (T) and space parity (P) [3,4]. An experiment to search for the P,T-odd property of the electron, i.e. its electric dipole moment or eEDM, using trapped PbF molecules is currently under consideration [3]. Another experiment for the P,T-odd property of the electron, i.e. without any artificial parameters. This is important for verifying the nature of the new terms introduced in the present paper, the parameters of the spin-rotational Hamiltonian are obtained in two different ways, from fitting the experimentally observed transitions and from ab initio calculations.

In the present paper the hyperfine structure of rotational levels of the $^2\Pi_{\pm 1/2}$ electronic state is obtained by numerical diagonalization of the molecular Hamiltonian ($\mathbf{H}_{\text{mol}}$) on the basis set of the electronic-vibrational-rotational wavefunctions.

\begin{align}
\chi(R,J)\Psi_{2\Pi_{\pm 1/2}}(\alpha,\beta)^F U_{M_F}^F U_{M_R}^R ,
\end{align}

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The vibrational wavefunction is $\chi(R,J)$ and it is determined by the equation

\begin{align}
\chi(R,J) = \frac{1}{\sqrt{2J+1}} \left( -\frac{\hbar^2 d^2}{2M_r dR^2} + \frac{\hbar^2 J(J+1)}{2M_r R^2} + V(R) \right) \chi_J = E_J \chi_J .
\end{align}

Here $\theta_{M_F,\Omega}^{\alpha,\beta} = \sqrt{(2J+1)/4\pi} \mathcal{D}^{J}_{M_F,\Omega}(\alpha,\beta,\gamma=0)$. The rotational wavefunction and $U_{M_F}^F$ are the nuclear spin wavefunctions on F and Pb for $^{207}$Pb$^{19}$F. For even $^{207}$Pb$^{19}$F, the nuclear spin wavefunction on Pb $U_{M_I}^Pb = 1$. The scheme of the calculation is similar to that in [8], although here we additionally introduce J-dependence for the vibrational wave functions. As one can see below, this is required to reproduce the experimental transition energies of the $^2\Pi_{\pm 1/2}$ state.

**Electronic Structure Calculations**

A series of ab initio calculations was performed in the present paper. To compute the hyperfine structure constants of the PbF molecule a scheme which combines the generalized relativistic effective core potential (GRECP) approach [9,10] with the non-variational restoration procedure [11] was used. The “two-step” approach has recently been used in [8,12,13] for the calculation of other “core properties” (such as effective electric field on electron, Schiff moment enhancement factor etc.) in molecules and atoms.

To compute the hyperfine structure constants for the ground and excites states of PbF, fully-relativistic Fock-space coupled cluster code with single and double cluster amplitudes (FS-RCCSD) [10,17] was applied. In this calculation both the valence and outer-core ($5s^25p^63d^{10}6s^26p^2$) electrons of Pb and all the electrons...
of F (i.e. 31-electrons in total) were treated explicitly while the inner-core electrons of Pb were excluded using the GRECP method.

To calculate the Pb hyperfine parameters, a basis set consisting of $8s$, $7p$, $4d$, $1f$ and $1g$ ([8,7,4,1,1]) contracted Gaussian basis functions on Pb and $5s$, $4p$, $2d$, $1f$ ([5,4,2,1]) functions on F was used. To calculate the F hyperfine parameters the basis set on Pb was reduced to [8,6,3,1], while the basis set on F was increased to [7,6,3,1]. The original set of basis functions on Pb was frozen as spinors [10] using the GRECP technique. The outer-core electrons of Pb consisting of $8s$ while the inner-core electrons of Pb were treated in this calculation. The outer-core electrons of Pb were frozen as spinors [10] using the GRECP technique.

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**MOLECULAR HAMILTONIAN**

We represent the molecular Hamiltonian as

$$H_{\text{mol}} = H_{\text{rot}} + H_{\text{hfs}} + H_1.$$ 

Here $H_{\text{rot}}$ is the rotational Hamiltonian and $H_{\text{hfs}}$ is the hyperfine interaction between electrons and nuclei. $H_1$ includes the nuclear spin – rotational interaction and also effectively takes into account the $H_{\text{rot}}$ and $H_{\text{hfs}}$ interactions between $2\Pi_{\pm1/2}$ and other electronic states. For $H_1$ we have

$$H_1 = c_1 I_1 \cdot J + c_2 I_2 \cdot J + c_0 I_1 \cdot I_2.$$ 

The parameters required to calculate the matrix elements of $H_{\text{rot}}$ and $H_{\text{hfs}}$ in the basis set [2] are determined by equations (5) - (14):

$$E_J = B \cdot J(J + 1) - D \cdot [J(J + 1)]^2,$$

$$p_J = \frac{\hbar^2}{M_r R^2} \langle \chi_J \langle \Psi_{2\Pi_{1/2}} | J^e_r | \Psi_{2\Pi_{-1/2}} \rangle \chi_J \rangle,$$

where $p_J \equiv p + p_D \cdot J(J + 1)$,

$$\hat{\rho} = 2B \langle \Psi_{2\Pi_{3/2}} | J^e_+ | \Psi_{2\Pi_{1/2}} \rangle,$$

$$A_{J||n} = \frac{\mu_F(Pb)}{I \Omega} \langle \chi_J \langle \Psi_{2\Pi_{1/2}} | \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \mid \Psi_{2\Pi_{1/2}} \rangle \chi_J \rangle,$$

where $A_{J||n} \equiv A_{||n} + A_{D||n} \cdot J(J + 1),$ (11)

$$A_{J\pm n} = \frac{\mu_F(Pb)}{I \Omega} \langle \chi_J \langle \Psi_{2\Pi_{1/2}} | \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \mid \Psi_{2\Pi_{-1/2}} \rangle \chi_J \rangle,$$ (12)

$$\hat{A}_{\pm n} = \frac{\mu_F(Pb)}{I \Omega} \langle \Psi_{2\Pi_{3/2}} | \sum_i \left( \frac{\alpha_i \times r_i}{r_i^3} \right) \mid \Psi_{2\Pi_{1/2}} \rangle.$$ (14)

Here $p_D$, $A_{||n}$, and $A_{D||n}$ are centrifugal corrections to the corresponding parameters, $p$, $A_{||n}$, and $A_{\pm n}$. Note that $n=1$ for F and $n=2$ for $^{207}$Pb. To evaluate the vibration-rotation energies, $E_J$, and wavefunctions, $\chi_J$, the Schrödinger equation (3) was solved for the ground state wavefunctions $\Psi$ in the basis set (2) are determined by equations (12), (13) and (14) over the $\chi_J$ wavefunctions were evaluated and the $p$, $p_D$, $A_{||n}$, $A_{D||n}$ parameters were fitted using eqs. (5), (11) and (13). Parameters $\hat{\rho}$ and $\hat{A}_{\pm n}$ (eqs. (8) and (14)) were computed using only the electronic wavefunction calculated at $R = 3.9$ a.u.

**RESULTS AND DISCUSSION**

As mentioned above, the parameters of the molecular effective spin-rotational Hamiltonian for PbF were determined in the present work both by fitting the experimentally observed transitions and on the basis of ab initio calculations of the $\Psi_{2\Pi_{1/2}}$ and $\Psi_{2\Pi_{3/2}}$ states. To clarify the relative role of the different parameters we have performed several fits with some parameters fixed to zero. The parameters thus obtained are listed in Tables II and III. The calculated parameters agree reasonably well with the fitted ones. The present $A_{||2} = 9796$ MHz and $A_{\pm 2} = -6911$ MHz values are in a good agreement with those obtained in paper [5], which were found to be 9727 MHz and $-6860$ MHz, respectively. In this paper we use a larger basis set and the FS-RCCSD method for electronic structure calculations instead of the SODCI method used in [5]. Besides, in the latter paper the $A_{||2}$ and $A_{\pm 2}$ values were evaluated using the only electronic wavefunction obtained at $R = 4.0$ a.u., whereas in the present paper they are obtained from eqs. (11) and (13), respectively. The deviations of our fits from the observed microwave
transitions are given in Table III for $^{208}$Pb$^{19}$F and in Table IV for $^{207}$Pb$^{19}$F. The error was defined as

$$\sum_{i=1}^{N_t} \frac{(\nu_{fit} - \nu_{obs})^2}{\delta_i},$$  \hspace{1cm} (15)$$

where $N_t$ is the number of measured transitions and $\delta_i$ is the experimental error for a given transition. In fit 1 for the $^{208}$Pb$^{19}$F the parameters $\tilde{p}$, $A_{\perp\perp}$, $A_{D||1}$, and $A_{D\perp}$ are fixed to zero. Note that the parameters $\tilde{p}$ and $A_{\perp\perp}$ take into account the interactions of $H_{rot}$ and $H_{hf}$, respectively, with the $2\Pi_{\pm3/2}$ electronic state. In the cases of fit 2, fit 3 and fit 4 we sequentially include parameters $\tilde{p}$, $A_{\perp\perp}$ and $A_{D||1}$ with $A_{D\perp}$. Data from Table III show that accuracy for the cases of fit 2 and fit 3 is actually the same as for fit 1. Note that the inclusion of the $\tilde{p}$ and $A_{\perp\perp}$ parameters strongly influence the $c_1$ parameter. This is in agreement with the fact that $c_1$, in particular, takes into account the $H_{rot}$ and $H_{hf}$ interactions between the $2\Pi_{\pm1/2}$ and $2\Pi_{\pm3/2}$ electronic states.

On the other hand, one can see that parameters $A_{D||n}$ and $A_{D\perp n}$ are important and that their inclusion allows one to reproduce transition energies within the experimental accuracy. In fit 5 we keep $A_{D||1}$ and $A_{D\perp}$ while removing the $\tilde{p}$ and $A_{\perp\perp}$ parameters. This only slightly influences on accuracy of the fit.

For $^{207}$Pb$^{19}$F we have performed the following fits. In fit 1 all the parameters were used. In fit 2 we have excluded the parameters corresponding to interactions with the $2\Pi_{\pm3/2}$ electronic states. Data from Table IV show that this does not influence the accuracy of the fit.

In fits 1 and 2 for $^{208}$Pb$^{19}$F and in fits 4 and 5 for $^{207}$Pb$^{19}$F we have included centrifugal corrections for both $A_{\perp\perp}$ and $A_{\perp\perp}$ parameters. However, it is clear from general theory (see eq. (2) in Ref. 4 and eq. (2) in Ref. 22) that for a $2\Pi_{\pm1/2}$ state $A_{\perp\perp}$ is the leading term, and the $J$-dependence of the hyperfine splitting shows that the contribution due to $A_{\perp\perp}$ is further reduced as $J$ increases. Of course the centrifugal corrections become more important at higher $J$, where the relative influence

| TABLE I. Parameters used to obtain the pure rotational spectra for $^{208}$Pb$^{19}$F |
|---|---|---|---|---|---|---|
| fit | 1 | 2 | 3 | 4 | 5 | 6 |
| B (cm$^{-1}$) | 0.228027888 | 0.228034349 | 0.228034349 | 0.228034349 | 0.228027888 | 0.228027888 |
| D × 10$^7$ (cm$^{-1}$) | 1.855 | 1.855 | 1.855 | 1.855 | 1.855 | 1.856 |
| p (cm$^{-1}$) | -0.138214051 | -0.138214052 | -0.138214052 | -0.138214042 | -0.138214041 | -0.138214041 |
| pD × 10$^7$ (cm$^{-1}$) | -1.020 | -1.020 | -1.020 | -1.037 | -1.037 | -1.037 |
|  \tilde{p} (cm$^{-1}$) | fixed to zero | 0.4625 | 0.4625 | 0.4625 | fixed to zero | fixed to zero |
| $A_{\perp\perp}$ (MHz) | 409.906 | 409.906 | 409.906 | 409.919 | 409.919 | 409.906 |
| $A_{D||1}$ × 10$^4$ (MHz) | fixed to zero | fixed to zero | fixed to zero | fixed to zero | -1.3 | -2.9 |
| $A_{\perp\perp}$ (MHz) | 255.9936 | 255.9935 | 255.9935 | 255.9912 | 255.9911 | 255.9911 |
| $A_{D||1}$ × 10$^4$ (MHz) | fixed to zero | fixed to zero | fixed to zero | fixed to zero | 5.2 | 5.3 |
| $c_1$ (MHz) | 0.0095 | 0.0095 | 0.0095 | 0.0095 | 0.0095 | 0.0095 |
| $A_{\perp\perp}$ (MHz) | fixed to zero | fixed to zero | fixed to zero | fixed to zero |

| TABLE II. Parameters used to obtain the pure rotational spectra for $^{207}$Pb$^{19}$F |
|---|---|---|---|---|---|
| fit | 1 | 2 | 3 | calc. |
| B (cm$^{-1}$) | 0.228126407 | 0.228119947 | 0.228119945 | 0.228 |
| D × 10$^7$ (cm$^{-1}$) | 1.865 | 1.867 | 1.869 | 1.83 |
| p (cm$^{-1}$) | -0.138270134 | -0.138270134 | -0.138270110 | -0.140 |
| pD × 10$^7$ (cm$^{-1}$) | -1.102 | -1.101 | -1.098 | |
|  \tilde{p} (cm$^{-1}$) | 0.4625 | fixed to zero | fixed to zero | 0.368$^a$ |
| $A_{\perp\perp}$ (MHz) | 409.910 | 409.897 | 409.896 | 437 |
| $A_{D||1}$ × 10$^4$ (MHz) | -0.2 | -5.4 | fixed to zero | -4.9 |
| $A_{\perp\perp}$ (MHz) | 255.9921 | 255.9920 | 255.9919 | 232 |
| $A_{D||1}$ × 10$^4$ (MHz) | 4.5 | 4.5 | 4.7 | 7.1 |
| $c_1$ (MHz) | 0.0051 | 0.0095 | 0.0095 | |
| $A_{\perp\perp}$ (MHz) | 153 | fixed to zero | fixed to zero | 166$^a$ |
| $A_{D2}$ (MHz) | 10146.5957 | 10146.6691 | 10146.6697 | 9796 |
| $A_{D||2}$ × 10$^4$ (MHz) | 5.7 | 5.7 | fixed to zero | 5.8 |
| $A_{\perp\perp}$ (MHz) | -7624.0375 | -7624.0375 | -7624.0381 | -6911 |
| $A_{D||2}$ × 10$^4$ (MHz) | -6.4 | -6.4 | -6.5 | -5.9 |
| $c_2$ (MHz) | 0.0617 | 0.0367 | 0.0375 | |
| $A_{D2}$ (MHz) | -896 | fixed to zero | fixed to zero | -1217$^a$ |
| $c_0$ (MHz) | 0.0011 | 0.0013 | 0.0015 | |

$^a$ This parameter was calculated in 13-electron approximation using SODCI method (see text).
TABLE III. Observed pure rotational transition frequencies $v_{obs}$ of the $X_1$ state of $^{208}$Pb$^{19}$F. The deviation of n-th fit is given by $\Delta_n = \nu_{obs} - \nu_{fits}$.

| Levels  | $v_{obs}$  | $\Delta_1$ | $\Delta_2$ | $\Delta_3$ | $\Delta_4$ | $\Delta_5$ | $\Delta_6$ |
|---------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1-3     | 3922.0065(20)| -6          | -10         | -10         | -9          | -5          | -5          |
| 2-4     | 4194.7773(7) | -1          | 0           | 0           | 3           | 3           | 1           |
| 1-4     | 4229.7176(30)| 15          | 29          | 29          | 19          | 20          | 19          |
| 6-7     | 8117.3017(10)| -8          | -6          | -5          | -5          | -5          | -5          |
| 5-7     | 8199.8478(9) | 4           | 6           | 7           | 7           | 6           | 5           |
| 6-8     | 8307.5180(20)| -2          | 8           | 9           | 8           | 6           | 6           |
| 5-8     | 8390.0664(20)| -12         | -3          | -3          | -7          | -7          | -7          |
| 10-11   | 12277.6822(7)| 1           | 12          | 13          | 3           | 3           | 3           |
| 9-12    | 12540.8465(8)| -5          | -17         | -17         | -17         | -13         | -13         |
| 14-15   | 16482.5160(10)| 2           | 11          | 11          | -2          | -2          | -2          |
| 13-16   | 16688.4929(20)| 17          | -35         | -36         | -36         | 10          | 10          |
| 1-5     | 1841.5880(5) | 1           | 5           | 5           | 2           | 2           | 2           |
| 2-6     | 18462.1933(5)| 2           | -7          | -7          | -8          | 0           | 0           |
| 1-6     | 18497.1352(5)| 2           | 6           | 5           | 6           | 1           | 1           |
| 4-7     | 22384.7171(5)| 1           | -7          | -7          | -6          | -2          | -2          |
| 4-8     | 22574.9344(5)| -2          | -3          | -3          | -1          | -1          | 0           |
| 3-7     | 22691.9306(5)| 2           | 8           | 8           | 7           | 1           | -1          |
| Error   | 1.86 4.84 4.83 4.82 1.60 1.62 1.63 |

of the $A_{\parallel n}$ terms is quite important. Hence the inclusion of the $A_{D\parallel n}$ centrifugal correction parameters should be less important to the fits than $A_{D\parallel n}$. To confirm this we have performed fit 6 for $^{208}$Pb$^{19}$F and fit 3 for $^{207}$Pb$^{19}$F where we have excluded the $A_{D\parallel n}$ parameters. Data in Tables III and IV show that this does not influence the accuracy of the fits.

In paper [6], new $d_{c1}$ and $d_{c2}$ parameters were introduced to fit the spectra of PbF. Two possibilities were given for their origin. Our parameters $A_{D11}$ and $A_{D12}$ are also required to fit the spectra of PbF and are in robust agreement within experimental uncertainty with $d_{c1}$ and $d_{c2}$, which were found to be .00056(10) MHz and $-0.007(2)$ MHz, respectively. Therefore, we suggest that parameters $d_{c1,2}$ can be rather treated as centrifugal corrections to the $A_{11,2}$ parameters in accordance with the second interpretation given in [7].

This work is supported by the SPbU Fundamental Science Research grant from Federal budget No. 0.38.6520.13 and RFBR Grant No. 13-02-01406. L.S. is also grateful to the Dmitry Zimin “Dynasty” Foundation. The molecular calculations were performed at the Supercomputer “Lomonosov”. R.J.M. would like to acknowledge support from Pomona College and the German Academic Exchange Service (DAAD).

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