Zeeman interaction in $^3\Delta_1$ state of HfF$^+$ to search for the electron electric-dipole-moment

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We report the theoretical investigation of the suppression of magnetic systematic effects in HfF$^+$ cation for the experiment to search for the electron electric dipole moment. The $g$-factors for $J = 1, F = 3/2, |M_F| = 3/2$ hyperfine levels of the $^3\Delta_1$ state are calculated as functions of the external electric field. The lowest value for the difference between the $g$-factors of $\Omega$-doublet levels, $\Delta g = 3 \times 10^{-6}$, is attained at the electric field 7 V/cm. The body-fixed $g$-factor, $G_{||}$, was obtained both within the electronic structure calculations and with our fit of the experimental data from H. Loh, K. C. Cossel, M. C. Grau, K.-K. Ni, E. R. Meyer, J. L. Bohn, J. Ye, and E. A. Cornell, Science 342, 1220 (2013). For the electronic structure calculations we used a combined scheme to perform correlation calculations of HfF$^+$ which includes both the direct 4-component all-electron and generalized relativistic effective core potential approaches. The electron correlation effects were used during the coupled cluster methods. The calculated value $G_{||} = 0.0115$ agrees very well with the $G_{||} = 0.0118$ obtained in the our fitting procedure. The calculated value $D_{||} = -1.53$ a.u. of the molecule frame dipole moment (with the origin in the center of mass) is in agreement with the experimental value $D_{||} = -1.54(1)$ a.u. [H. Loh, Ph.D. thesis, Massachusetts Institute of Technology (2006)].

INTRODUCTION

Search for the electron electric dipole moment (eEDM), $d_e$, is important test of the standard model and its extensions [1, 2]. The best current limit on the electron EDM, $|d_e| < 9 \times 10^{-29}$ e·cm was set with a molecular beam of the thorium monoxide (ThO) molecules by ACME collaboration [3] using the theoretical data from Refs. [4, 5]. A number of other systems are considered to search for the eEDM and other manifestations of effects of time-reversal (T) and spatial parity (P) symmetries violation of the fundamental interactions: ThO [4, 8], TaN [7, 8], ThF$^+$ [10, 11], PbF [12–15], WC [16, 17], RaO [18, 19], RaF [20, 21], PtH [22, 23], etc.), TIF [24] molecules and cations.

E. Cornell’s group has suggested to use the trapped molecular ions for the eEDM search [22, 28]. One of the most promising systems for the search is the HfF$^+$ cation [10, 22, 29, 32] which is also of interest for other fundamental experiments [34, 35]. It has the long-lived metastable $^3\Delta_1$ electronic state with lifetime $\approx 2s$ [29, 31] which means a very large coherence time is achievable in the experiment. The other main feature of the $^3\Delta_1$ state is that it has a very small $g$-factor (zero in nonrelativistic limit in approximation with free-electron $g$-factor, $g_S$, equal to -2.0) which leads to the suppression of the magnetic systematic effects. It was shown that further suppression of systematics is possible due to existence of the $\Omega$-doublet structure of molecules in the $^3\Delta_1$ electronic state [36, 37]. For preparation and implementation of the eEDM experiment one should investigate the dependence of upper and lower $\Omega$-doublet states $g$-factors on the strength of the laboratory electric field. And this is the goal of the present paper.

THEORY

We define the $g$-factors such that Zeeman shift is equal to

$$E_{\text{Zeeman}} = -g \mu_B B M_F,$$

(1)

where $\mu_B$ is the Bohr magneton, $M_F$ is the projection of the total angular momentum on the $z$ axis, $B = B\hat{z}$ is the external magnetic field. This definition matches the ones in the papers [10, 37]. Using the angular momentum algebra [40], one can calculate that in the adiabatic approximation and in the limit of zero hyperfine interaction $g$-factors of hyperfine sublevels of the $^3\Delta_1$ state of HfF$^+$ are determined by

$$g = -G_{||} F(F + 1) + J(J + 1) - 3/4$$
$$2F(F + 1)J(J + 1) +$$

(2)

$$g_F \frac{\mu_N}{\mu_B} F(F + 1) - J(J + 1) + 3/4$$
$$2F(F + 1)$$

(3)

Here $g_F = 5.25773$ is $^{19}$F nucleus $g$-factor, $\mu_N$ is the nuclear magneton. The first term in the right hand side of Eq. (3) is the electronic contribution [41] and the second term is contribution from the magnetic moment of $^{19}$F nucleus.

Eq. (3) does not take into account the hyperfine interaction between different rotational levels and nonadiabatic interaction with other electronic states. To take these effects into account, following Refs. [37, 41], the
g-factors are obtained by numerical diagonalization of the molecular Hamiltonian ($\hat{H}_{\text{mol}}$) in external electric $\mathbf{E} = E\hat{z}$ and magnetic $\mathbf{B} = B\hat{z}$ fields over the basis set of the electronic-rotational wavefunctions

$$
\Psi_{\Omega}\theta_{M,\Omega}^{J}(\alpha, \beta)U_{M}^{J}.
$$

(4)

Here $\Psi_{\Omega}$ is the electronic wavefunction, $\theta_{M,\Omega}^{J}(\alpha, \beta, \gamma = 0)$ is the rotational wavefunction, $\alpha, \beta, \gamma$ are Euler angles, $U_{M}^{J}$ is the F nuclear spin wavefunctions and $M$ ($\Omega$) is the projection of the molecule angular momentum on the lab $\hat{z}$ (internuclear $\hat{n}$) axis, $M_f = \pm 1/2$ is the projection of the nuclear angular momentum on the same axis. Note that $M_F = M_I + M$.

We represent the molecular Hamiltonian for $^{180}$Hf$^{9}$F$^+$ as

$$
\hat{H}_{\text{mol}} = \hat{H}_{\text{el}} + \hat{H}_{\text{rot}} + \hat{H}_{\text{hfs}} + \hat{H}_{\text{ext}}.
$$

(5)

Here $\hat{H}_{\text{el}}$ is the electronic Hamiltonian,

$$
\hat{H}_{\text{rot}} = B_{\text{rot}}J^2 - 2B_{\text{rot}}(\mathbf{J} \cdot \mathbf{J})
$$

is the rotational Hamiltonian,

$$
\hat{H}_{\text{hfs}} = g_F\mathbf{I} \cdot \sum_i \left( \alpha_i \times \mathbf{r}_i \right)
$$

(7)

is the hyperfine interaction between electrons and fluoride nuclei,

$$
\hat{H}_{\text{ext}} = \mu_B(\mathbf{L}^e - g_S\mathbf{S}^e) \cdot \mathbf{B} + g_F\frac{\mu_N}{\mu_B} I \cdot \mathbf{B} - \mathbf{D} \cdot \mathbf{E}
$$

(8)

describes the interaction of the molecule with external magnetic and electric fields, $B_{\text{rot}} = 0.2989$ [29] is the rotational constant, $g_S = -2.0023$ is a free-electron $g$-factor, $\mathbf{D}$ is the dipole moment operator.

For the current study we have considered the following low-lying electronic basis states: $3\Delta_1$, $3\Delta_2$, $3\Pi_0^+$ and $3\Pi_0^-$. $\hat{H}_{\text{el}}$ is diagonal on the basis set [41]. Its eigenvalues are transition energies of these states. They were calculated and measured in Ref. [29]:

$$
3\Delta_1: T_e = 976.930 \text{ cm}^{-1},
$$

$$
3\Delta_2: T_e = 2149.432 \text{ cm}^{-1},
$$

$$
3\Pi_0^- : T_e = 10212.623 \text{ cm}^{-1},
$$

$$
3\Pi_0^+ : T_e = 10401.723 \text{ cm}^{-1}.
$$

(9)

Other terms of molecular Hamiltonian $\hat{H}_{\text{mol}}$ are determined by parameters given by Eqs. [10] - [21] below. We have performed electronic calculations for the following matrix elements of the basis electronic states:

$$
G_{\Delta_1}^{(3)} = \langle 3\Delta_1 | \hat{L}_z^e - g_S \hat{S}_z^e | 3\Delta_2 \rangle = -2.617,
$$

(10)

$$
D_{\Delta_1}^{(3)} = \langle 3\Delta_1 | \hat{D}_-^e | 3\Delta_2 \rangle = 0.034 \text{ a.u.},
$$

(11)

$$
\Delta^{(3)} = 2B_{\text{rot}}(3\Delta_1 | J_z^e | 3\Delta_2) = -7370874 \text{ cm}^{-1},
$$

(12)

$$
D_{\parallel}^{(3)} = \langle 3\Delta_1 | \hat{D}_n^e | 3\Delta_1 \rangle = -1.53 \text{ a.u.},
$$

(13)

$$
D_{\perp}^{(2a)} = \langle 3\Delta_1 | \hat{D}_+^{(3)} | 3\Pi_0^+ \rangle = 0.457 \text{ a.u.},
$$

(14)

$$
D_{\perp}^{(2b)} = \langle 3\Delta_1 | \hat{D}_+^{(3)} | 3\Pi_0^- \rangle = 0.447 \text{ a.u.}
$$

(15)

Matrix element [14] is in a good agreement with the value $D_{\perp}^{(2a)} = 0.467 \text{ a.u.}$ calculated in Ref. [31]. Calculated permanent dipole moment $D_{\parallel}$ is in a good agreement with the experimental value $D_{\parallel} = -1.54(1) \text{ a.u.}$ [42]. Matrix elements

$$
G_{\perp}^{(3)}(\Delta_1) = \langle 3\Delta_1 | \hat{L}_z^e - g_S \hat{S}_z^e | 3\Pi_0^- \rangle = 1.3456,
$$

(16)

$$
G_{\perp}^{(3)}(\Delta_1) = \langle 3\Delta_1 | \hat{L}_z^e - g_S \hat{S}_z^e | 3\Pi_0^- \rangle = 1.5524,
$$

(17)

$$
\Delta^{(3)} = 2B_{\text{rot}}(3\Delta_1 | J_z^e | 3\Pi_0^-) = 0.8044 \text{ cm}^{-1},
$$

(18)

$$
\Delta^{(3)} = 2B_{\text{rot}}(3\Delta_1 | J_z^e | 3\Pi_0^-) = 0.9280 \text{ cm}^{-1}
$$

(19)

were chosen in such a way to reproduce the experimental value $0.369 \cdot J(J+1) \text{ MHz}$ for $\Omega$ doubling of $3\Delta_1$. Matrix element

$$
A_{\parallel} = g_F \langle \Psi_{3\Delta_1} | \sum_i \left( \frac{\alpha_i \times \mathbf{r}_i}{r_i^3} \right) \rangle | \Psi_{3\Delta_1} \rangle = -58.1 \text{ MHz}
$$

(20)

were taken from Ref. [31]. Hyperfine structure only of the $3\Delta_1$ state was taken into account. $G_{\parallel}$ is given by the following formula:

$$
G_{\parallel} = \frac{1}{\Omega} \langle 3\Delta_1 | \hat{L}_n^e - g_S \hat{S}_n^e | 3\Delta_1 \rangle.
$$

(21)

To perform electronic structure calculations of the diagonal matrix elements [13] and [21] we have used the combined computational scheme similar to that used in Refs. [8, 33, 43] which includes electronic structure treatment within the generalized relativistic effective core (GRECP) potential approach [44, 45] and the direct relativistic 4-component Dirac-Coulomb(-Gautn) approach. This scheme includes the following stages: (i) 2-component 52-electron relativistic correlation calculation using the coupled cluster with single, double and noniterative triple cluster amplitudes, (CCSD(T), method. For this we have used the semilocal version of the 44-electron GRECP operator [44, 45]. The 28 inner core 1s, 3d electrons of Hf have been excluded from the correlation treatment by the GRECP operator and all other (outer core and valence) electrons were included in the correlation calculation. (ii) To treat the correlation contribution from the inner core electrons we have performed direct 4-component calculations at the level of the coupled cluster with single amplitudes (CCS) method as the difference in the calculated properties within the 80-electron (i.e., all-electron) CCS versus the 52-electron CCS. (iii) Calculation of vibration correction for $G_{\parallel}$. (iv) Calculation of the correction on high order correlation effects.

For the stage (i) we have generated the uncontracted basis set for Hf that includes 25 $s$-, 25 $p$-, 21 $d$-, 14 $f$-, 10 $g$-, 5 $h$- and 5 $i$- type Gaussians For fluorine the (13,7,4,3,2)/[6,5,4,3,2] aug-ccpVQZ basis set [46, 47] was used. Note that the reduction of the basis set on Hf to 15 $s$-, 10 $p$-, 8 $d$-, 7 $f$-, 4 $g$-, 2 $h$- and 1 $i$- type Gaussians (only $g$-, $h$- and $i$- type basis functions were
contracted using the code from Ref. 48) leads only to slight changes in the calculated values. For the stage (ii) the CVDZ 49, 50 basis set for Hf and the cc-pVDZ 46, 47 basis set for F were used. In the stage (iv) the high order correlation effects were considered as a difference in the values of considered properties calculated within the coupled cluster with single, double, triple and noniterative quadruple amplitudes and the CCSD(T) method. In the calculations 20 valence and outer core electrons of HfF⁺ were correlated.

To calculate off-diagonal matrix elements 10, 11 and 12 we have used 12-electron version of the GRECP operator for Hf used earlier in Refs. 30, 31, 34 to perform 2-component 20-electron correlation calculations. For the calculations we have used the [12,16,16,10,8]/(6,5,5,3,1) basis set for Hf and [14,9,4,3]/(4,3,2,1) ANO-I basis set for F 51. Calculations of the matrix elements 10, 11 and 12 were performed within the linear-response coupled cluster with single and double cluster amplitudes, LR-CCSD, method.

Electronic calculations were performed within the 52 and 53 codes. The code to calculate matrix elements of the g-factor operator over the 4-component molecular bispinors has been developed in the present paper.

RESULTS AND DISCUSSIONS

\( G_\parallel \) obtained from the electronic structure calculation is equal to 0.0115 and is in very good agreement with the value \( G_\parallel = 0.011768 \) obtained by fitting the \( g_{\text{fit}} = -0.00306 \) value. In Ref. 10 the experimental value \( g_{\exp} = +0.00306 \) obtained in the external electric field \( E = 11.6 \, V/cm \) is given. The electronic structure calculation is in agreement with the experiment only if the sign of \( g \)-factor will be changed. Thus, for consistency with the experiment, in this work we further use the \( g \)-factor value \( g_{\text{fit}} = -g_{\exp} \) with the sign reversed from that in Ref. 10. Only \( G_\parallel \) parameter was optimized in the fitting procedure. Eq. 3 gives \( G_\parallel = 0.012043 \).

In Fig. 1 the calculated \( g \)-factors for the \( J = 1, F = 3/2, M_F = 3/2 \) levels of HfF⁺ \( ^3\Delta_1 \) state are shown as functions of the laboratory electric field. The calculated difference \( \Delta g = g^u - g^l = 3.4 \times 10^{-6} \) between the \( g \)-factors of the upper \( (g^u) \) and lower \( (g^l) \) levels of \( \Delta_1 \) doublet is in a good agreement with the experimental value \( -1(2) \times 10^{-5} \) 10. Note, that the difference is zero in the adiabatic approximation. The lowest value for the difference, \( \Delta g = 3 \times 10^{6} \), is attained at the electric field \( E = 7 \, V/cm \). The smaller \( \Delta g \), the smaller are the systematics \( \mu_B \Delta g \tilde{B} \) coming from a spurious magnetic field \( \tilde{B} \).

FIG. 1. (Color online) Calculated \( g \)-factors for upper \((g^u)\) and lower \((g^l)\) levels of \( \Omega \) doublets for the \( J = 1, F = 3/2, M_F = 3/2 \) levels of the \(^3\Delta_1\) state of HfF⁺ as functions of the electric field.

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