Laser-cooled HgF as a promising candidate to measure the electric dipole moment of the electron

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In order to realize more sensitive measurement of the electron's electric dipole moment (*e*EDM), it would be worthwhile to find new laser-cooled molecules with large internal effective electric field (E_{eff}), high electric polarizability, and long lifetime of the *e*EDM measurement state. Here we demonstrate the theoretical feasibility of laser cooling and trapping the mercuric monofluoride ($^{202}Hg^{19}F$, $X^2\Sigma_{1/2}$) radicals, as well as their application in the *e*EDM measurement. We investigated the electronic, rovibrational, and hyperfine structures and verified the highly diagonal Franck-Condon factors of the main transitions by the Rydberg-Klein-Rees inversion method and the Morse approximation. Hyperfine manifolds of the $X^2\Sigma_{1/2}$ ($\upsilon = 0$) rotational states were examined with the effective Hamiltonian approach and a feasible sideband modulation scheme was proposed. In order to enhance optical cycling, the microwave remixing method was employed to address all the necessary levels. The Zeeman effect and the hyperfine structure magnetic *g* factors of the $X^2\Sigma_{1/2}$ ($\upsilon = 0$, N = 1) state were studied subsequently. Finally, its statistical sensitivity for the *e*EDM measurement was estimated to be about $6 \times 10^{-32}e$ cm in the trap, indicating that $^{202}Hg^{19}F$ might be a promising laser-cooled *e*EDM candidate when compared with the most recent ThO result of $d_e = (4.3 \pm 3.1_{stat} \pm 2.6_{syst}) \times 10^{-30}e$ cm [V. Andreev *et al.* (The ACME Collaboration), Nature (London) **562**, 355 (2018)].

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I. INTRODUCTION

The measurement of the electron's electric dipole moment (*e*EDM) has been a platform for searching new physics beyond the standard model of elementary physics since the 1950s, as suggested by Purcell and Ramsey [1]. A nonzero *e*EDM value can be directly used to trace the origin of the CP violation [2]. An often-quoted value of *e*EDM in the standard model was predicted to be below $10^{-38}e$ cm, which is obviously far below the current experimental sensitivities [3–6]. However, many extensions to the standard model predict a much larger *e*EDM value, such as the supersymmetry variants and generic models [7,8], some of which are under direct test by experimental efforts with the recently published upper limit of $d_e < 1.1 \times 10^{-29}e$ cm [6].

Mainly due to their important features of large internal effective electric field (E_{eff}) and high electric polarizability, there have been numerous diatomic molecules and molecular ions with heavy nuclei that are examined theoretically and experimentally to probe the *e*EDM, among which some precise experimental results have been obtained with YbF [3], PbO [9], ThO [4,6], and HfF⁺ [5]. Besides those, diatomic molecules and molecular ions such as PbF [10], WC [11], RaF [12], HgX [13], ThF⁺ [14], and BaF [15] are under either theoretical investigation or experimental attempts. We stress that only the YbF [16], RaF [17], and BaF [18] radicals have been

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either experimentally or theoretically studied for their lasercooling capabilities, showing their competitive potentials in the *e*EDM measurement with much longer coherence time.

The HgF radical was found to have a large $E_{\rm eff}$ of about 104 GV/cm [13], larger than ThO with 84 GV/cm [19], YbF with 26 GV/cm [20], and HfF⁺ with 24 GV/cm [21]. In this paper, we investigate further on ²⁰²Hg¹⁹F about its laser-cooling features in the following aspects: (i) the simple hyperfine structure arising from the interactions between the electron spin (S = 1/2), nuclear rotation, and nuclear spin (I = 1/2) for the rotational N = 1 energy levels of the ground state; (ii) the highly diagonal Franck-Condon matrix between the electronic ground state and the electronically excited $C^2\Pi_{1/2}$ state; and (iii) strong spontaneous radiation decay rate ($\Gamma \approx 2\pi \times 23$ MHz) due to the short lifetime of the excited $C^2 \Pi_{1/2}$ state ($\tau \approx 6.93$ ns) [22]. Considering the dissociative nature of the unbound $A^2\Pi^+$ state, there is only one intermediate electronic state $B^2 \Sigma^+$ that participates in the allowed transitions. Here, we choose $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ as a cooling channel for the vast difference between the decay rates γ_{CX} and γ_{CB} (the transition frequency $\omega_{CX}/\omega_{CB} \approx 3$ and the transition dipole moment $d_{\rm CX}/d_{\rm CB} \approx 20$, $\gamma \propto \omega^3 d^2$, thus $\gamma_{CB}/\gamma_{CX} \approx 10^{-4}$ [22]). Therefore the existence of the intermediate state and the unwanted $B^2 \Sigma^+ \leftarrow C^2 \Pi_{1/2}$ leak will not limit the laser-cooling process significantly, but only make the optical cycling more complex. YO [23] and BaF [18] radicals were processed in a similar way for the existence of an intermediate electronic state. The lifetime of the $B^2\Sigma^+$ state is also very short ($\tau \approx 8.05$ ns), and the undesired leakage of $B^2 \Sigma^+ \leftarrow C^2 \Pi_{1/2}$ will decay rapidly to $|X, N = 0, 2, +\rangle$ because of selection rules; however, we can close these additional loss channels by microwave mixing of rotational states.

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FIG. 1. The proposed scheme to create a quasicycling transition for laser cooling of HgF. Solid black lines indicate the relevant electronic and vibrational level structure. Solid upward lines indicate the laser-driven transitions at the wavelengths $\lambda_{vv'}$. Solid dotted red lines indicate the spontaneous decays from the *C* state along with FCFs $f_{v'v}$. The dotted blue line indicates the undesired leakage of $B^2\Sigma^+ \leftarrow C^2\Pi_{1/2}$.

Hg atoms have been studied for precise measurement for decades such as optical lattice clocks [24] and permanent atomic EDM measurement [25], while the HgF radicals were investigated for spectral measurement and laser application [26–32]. In order to carry out *e*EDM measurement using the HgF molecular beam, the HgF radicals can be prepared via the reaction of Hg vapor with F_2 [27–29], and are then injected into a cryogenic helium gas cell, similar to the beamloaded buffer gas method involving NH radicals [33]. Other fluorine donors such as SF₆ [30,34], NF₃ [28], N₂F₄ [28], and XeF₂ [35] can also be considered. Another interesting method inspired by Dharmasena et al. [36] implies that an atomic fluorine source based on fluoride crystals of the group-II elements such as MgF₂ might be promising in producing HgF, which was demonstrated by Faubel et al. [37] and already incorporated in the production of PbF radicals by Shafer-Ray's group [38]. Since the decomposition temperature of HgF₂ crystal can reach as high as 650 °C [30], the HgF molecules could also be produced by directly cracking HgF₂ [30,31], or by introducing alkali-metal vapor to enhance the chemical reaction with HgF_2 [32].

II. VIBRATIONAL TRANSITIONS AND FRANCK-CONDON FACTORS BETWEEN $X^{2}\Sigma_{1/2}$ AND $C^{2}\Pi_{1/2}$ STATES

The vibrational branching ratios of a molecular system are represented by the Franck-Condon factors (FCFs) among the involved optical transitions. As illustrated in Fig. 1, we depicted the laser scheme and spontaneous decay based on the calculated transition wavelength $\lambda_{vv'}$ and the corresponding FCFs $f_{v'v}$. The molecular parameters of the states $X^2 \Sigma_{1/2}$ and $C^2 \Pi_{1/2}$ used in the calculation are listed in Table I.



FIG. 2. Driving $|C, \upsilon' = 0, J' = 1/2, +\rangle \leftarrow |X, \upsilon = 0, N = 1, -\rangle$ transition will allow a spontaneous decay that only goes back to the N = 1 state. Unwanted $B^2 \Sigma^+ \leftarrow C^2 \Pi_{1/2}$ transition (not shown in the figure) will eventually end up with the $|X, N = 0, 2, +\rangle$ state. The $\Delta J = +1, \Delta F = +1$ microwave mixing transitions are used to close additional loss channels.

The FCFs of $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ transition were calculated with Rydberg-Klein-Rees (RKR) method [39] and Morse potential [40]. For the Morse potential method, the onedimensional analytical potential function is constructed using $U(x) = D[(1 - e^{-\beta x})^2 - 1]$ where $D = \hbar \omega_e^2 / 4 \omega_e \chi_e$ and $\omega_e \chi_e = \beta^2 \hbar / 2\mu$ (the potential is characterized by the depth D and the range β ; x, μ, ω_e , and $\omega_e \chi_e$ represent the position of the equilibrium point, the reduced mass, and the standard harmonic and anharmonic spectroscopic parameters, respectively). For the RKR method, the related potential-energy curves are numerically modeled by calculating classical turning points with vibrational and rotational spectroscopic constants.

The overlap integral $\langle \upsilon | \upsilon' \rangle$ and FCFs $|\langle \upsilon | \upsilon' \rangle|^2$ were calculated with respect to the wave functions of each involved vibrational state. Some of the FCFs are listed in Table II and their corresponding transition wavelengths were shown in Table III. The sum of f_{00} , f_{01} , and f_{02} is close to unity (~0.9999 for either method), which is very similar to the calculated results reported in Ref. [22] that the sum is larger than 0.9999; thus, almost 10⁴ photons can be scattered to slow the molecules. In fact, if the fourth laser beam is used, nearly 10⁵ photons can be scattered (the sum of f_{00} , f_{01} , f_{02} , and f_{03} is about 0.99999).

TABLE I. Parameters for the involved electronic states of HgF.

Molecular parameters	$X^{2}\Sigma_{1/2}$	$C^{2}\Pi_{1/2}$
$\overline{Te\left(\mathrm{cm}^{-1} ight)}$	0	39060 [26]
$\omega_e (\mathrm{cm}^{-1})$	490.8 [26]	468.6 [22]
$\omega_e \chi_e (\mathrm{cm}^{-1})$	4.05 [26]	10.33 [22]
r_e (Å)	2.110 [22]	2.092 [22]
τ (ns)		6.93 [22]

TABLE II. The calculated FCFs of HgF by the Morse potential method and the RKR inversion method.

Methods	f_{00}	f_{01}	f_{02}	f_{11}
Morse potential	0.9760	0.0204	0.0035	0.9540
RKR inversion	0.9615	0.0351	0.0033	0.8901

Based on the calculated results, $C^2 \Pi_{1/2}$ ($\upsilon' = 0$) \leftarrow $X^2 \Sigma_{1/2}$ ($\upsilon = 0$) transition was chosen as the main cooling transition due to its favorable FCFs ($f_{00} = 0.9615$), while the cooling laser wavelength is $\lambda_{00} = 256.10$ nm. The vibrational leakages can be addressed by repumping the $X^2 \Sigma_{1/2}$ (v = 1) directly to the $C^2 \Pi_{1/2}$ ($\upsilon' = 0$) as well as $\upsilon = 2$ to $\upsilon' =$ 1 with wavelengths $\lambda_{10} = 259.31 \text{ nm}$ and $\lambda_{21} = 259.48 \text{ nm}$, respectively. Theoretical results are in good agreement with experimental ones, as listed in Table III. Similar to the lasers used in the experimental system of Hg atoms [24,25], the laser used for HgF experiment can also be generated by frequency quadrupling laser diode systems or fiber lasers. For example, the main cooling laser of $\lambda_{00} = 256.10$ nm can be produced by a laser diode system or fiber laser operated at 1024.4 nm. A stable continuous-wave narrow-linewidth 253.7-nm fiber laser with 760 mW has been developed recently and the linewidth at 253.7 nm can reach as low as 100 kHz [41], opening up a possible solution of laser-cooling HgF radicals by the aid of a fiber laser with the desired wavelengths.

III. HYPERFINE STRUCTURE OF THE ²⁰²Hg¹⁹F MOLECULE

In this section, we will discuss the hyperfine structure of the lowest rotational levels of the $X^2 \Sigma_{1/2}$ state and the elimination of dark rotational states by the microwave remixing method. The discussion is very important for implementing nearly closed optical transitions. The $X^2 \Sigma_{1/2}$ state of HgF is a Hund's case (b) state while $C^2 \Pi_{1/2}$ is a Hund's case (a) state, therefore *N* is a good quantum number for $X^2 \Sigma_{1/2}$ but *J* is a good quantum number for $C^2 \Pi_{1/2}$. Considering the angular momentum and parity selection rules, the parities of the initial and final states of the transition should be opposite and $\Delta J = 0, \pm 1$. As a result, driving $|C, v' = 0, J' = 1/2, + \rangle \leftarrow |X, v = 0, N = 1, -\rangle$ transition will allow a spontaneous decay that will only go back to the N = 1 state.

For the ²⁰²Hg¹⁹F molecule, the total angular momentum operator $\hat{F} = \hat{N} + \hat{S} + \hat{I}$ in the ground $X^2 \Sigma_{1/2}$ state. Since $I_{\text{Hg}} = 0$ and $I_F = 1/2$, the spin-rotational and hyperfine interactions can split the $|X, v = 0, N = 1\rangle$ state into four

TABLE III. The comparison between the calculated and experimental results of the transition wavelengths of the $X^2 \Sigma_{1/2}$ and $C^2 \Pi_{1/2}$ states of HgF.

Transitions wavelength	Theoretical (nm)	Experimental (nm)
$\overline{\lambda_{00}}$	256.10	256.06 [26]
λ_{10}	259.31	259.24 [<mark>26</mark>]
λ_{21}	259.48	259.17 [<mark>26</mark>]

TABLE IV. Rotational and hyperfine structure parameters and the electric dipole moment for the $X^2 \Sigma_{1/2}$ ($\upsilon = 0$) state of 202 Hg 19 F.

Molecular parameters	$X^2\Sigma_{1/2}$	References
$B_{\nu}(cm^{-1})$	0.2181	[22]
$D_v (\mathrm{cm}^{-1})$	3.5081×10^{-7}	[22]
$\gamma_v (\mathrm{cm}^{-1})$	0.0143	[43]
$b_v (\mathrm{cm}^{-1})$	6.5×10^{-3}	[29]
$c_v({\rm cm}^{-1})$	0.0383	[29]
$\mu_{\rm e}\left({\rm D} ight)$	4.15	[44]

sublevels. For a nearly closed transitions scheme, all of the four hyperfine levels should be pumped simultaneously in order to prevent molecules from accumulating into one state. This can be realized by sideband modulation with commercial electro-optic modulators (EOMs).

The effective Hamiltonian describes all the involved intercouplings degrees of freedom in a molecular system. For the ²⁰²Hg¹⁹F $X^2 \Sigma_{1/2}$ state in particular, the effective Hamiltonian (H_{eff}) contains the molecular rotational term H_{R} , the spinrotational coupling H_{SR} , and the hyperfine interaction H_{hfs} . By the aid of the Frosch and Foley constants [42], we can then express

$$H_{\rm eff} = H_{\rm R} + H_{\rm SR} + H_{\rm hfs},\tag{1}$$

where $H_{\rm R} = B_{\nu}\hat{N}^2 - D_{\nu}\hat{N}^4$, $H_{\rm SR} = \Upsilon_{\nu}T^1(\hat{S})T^1(\hat{N})$, $H_{\rm hfs} = b_{\nu}T^1(\hat{I})T^1(\hat{S}) + c_{\nu}T^1_{q=0}(\hat{I})T^1_{q=0}(\hat{S}) + C_{\nu N}T^1(\hat{I})T^1(\hat{N})$, and $b_{F\nu} = b_{\nu} + c_{\nu}/3$. Here B_{ν} , D_{ν} , γ_{ν} , $b_{F\nu}$, and c_{ν} represent the molecular rotational constant, the centrifugal distortion constant, the spin-rotational coupling constant, the Fermi contact interaction constant, and the dipole-dipole interaction constant, respectively. $C_{\nu N}$ is negligibly small compared with other constants. The hyperfine parameters A_{\perp} and A_{\parallel} (195 and 1344 MHz) were measured by Knight, Jr. *et al.* [29]. Since $b_{\nu} = A_{\perp}$ and $c_{\nu} = A_{\parallel} - A_{\perp}$, the values of b_{ν} and c_{ν} were derived to be 195 MHz ($6.5 \times 10^{-3} \, {\rm cm}^{-1}$) and 1149 MHz ($0.0383 \, {\rm cm}^{-1}$), respectively. Rotational and hyperfine structure parameters as well as the electric dipole moment for the $X^2 \Sigma_{1/2}$ ($\nu = 0$) state of $^{202} {\rm Hg}^{19} {\rm F}$ are listed in Table IV.

With all the parameters mentioned above, the corresponding matrix elements for each term of the H_{eff} with the basis $|N, S, J, I, F, M_F\rangle$ are derived as

$$\langle N', S, J', I, F', M'_{F} | B_{\upsilon} \hat{N}^{2} - D_{\upsilon} \hat{N}^{4} | N, S, J, I, F, M_{F} \rangle$$

= $\delta_{N'N} \delta_{J'J} \delta_{F'F} \delta_{M'_{F}M_{F}} N(N+1) [B_{\upsilon} - D_{\upsilon} N(N+1)],$
(2)

TABLE V. Calculated frequencies for $\Delta J = +1$, $\Delta F = +1$ hyperfine transitions in the lowest rotational levels of the $X^2 \Sigma_{1/2}$ state.

N' - N	J'-J	F'-F	f (MHz)
1–0	3/2-1/2	1–0	13774.5865
		2-1	13262.1579
2-1	3/2 - 1/2	1-0	26148.6632
		2-1	25988.5968
	5/2-3/2	2-1	26354.7297
	. ,	3–2	26369.7489

$$\langle N', S, J', I, F', M'_F | \gamma_v T^1(\hat{S}) T^1(\hat{N}) | N, S, J, I, F, M_F \rangle$$

$$= \delta_{N'N} \delta_{J'J} \delta_{F'F} \delta_{M'_F M_F} \gamma_v (-1)^{N+J+S} [S(S+1)(2S+1)]^{1/2} [N(N+1)(2N+1)]^{1/2} \begin{cases} S N J \\ N S 1 \end{cases},$$
(3)

$$\langle N', S, J', I, F', M'_F | b_{\upsilon} T^1(\hat{I}) T^1(\hat{S}) | N, S, J, I, F, M_F \rangle$$

$$= \delta_{N'N} \delta_{F'F} \delta_{M'_F M_F} b_{\upsilon} (-1)^{J'+F+I+J+N+1+S} [(2J'+1)(2J+1)]^{1/2} [S(S+1)(2S+1)]^{1/2} [I(I+1)(2I+1)]^{1/2} \begin{cases} I \ J' \ F \\ J \ I \ 1 \end{cases} \begin{cases} J \ S \ N \\ S \ J' \ 1 \end{cases},$$
(4)

$$N', S, J', I, F', M_F | c_{\upsilon} T_{q=0}^{I}(I) T_{q=0}^{I}(S) | N, S, J, I, F, M_F \rangle$$

$$= \delta_{N'N} \delta_{F'F} \delta_{M'_F M_F} (-\sqrt{30}/3) c_{\upsilon} (-1)^{J'+F+I+N} [(2J'+1)(2J+1)]^{1/2}$$

$$\times [S(S+1)(2S+1)]^{1/2} [I(I+1)(2I+1)]^{1/2} (2N+1) \binom{N \ 2 \ N}{0 \ 0 \ 0} \begin{cases} I \ J' \ F \\ J \ I \ 1 \end{cases} \begin{cases} J \ J' \ 1 \\ N \ N \ 2 \\ S \ S \ 1 \end{cases},$$
(5)

and

$$\langle N', S, J', I, F', M'_F | C_{\nu N} T^1(\hat{I}) T^1(\hat{N}) | N, S, J, I, F, M_F \rangle = \delta_{N'N} \delta_{F'F} \delta_{M'_F M_F} C_{\nu N} (-1)^{2J+F'+I+N'+S+1} [N(N+1)(2N+1)]^{1/2} [I(I+1)(2I+1)]^{1/2} \times [(2J'+1)(2J+1)]^{1/2} \begin{cases} I & J & F' \\ J' & I & 1 \end{cases} \begin{cases} N & J & S \\ J' & N' & 1 \end{cases}.$$
(6)

Eigenvalues and eigenvectors were obtained by numerical diagonalization of the effective Hamiltonian matrix representations of the $X^2 \Sigma_{1/2}$ state. And the energy splittings between different rotational hyperfine levels are obtained and shown in Fig. 2. Once the hyperfine structure of the N = 1 state is clear, the sideband modulation scheme for the pumping laser to cover all the four hyperfine levels of the N = 1 level simultaneously can be proposed. For the $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ transition of 202 Hg¹⁹F, decay rate $\Gamma = 2\pi \times 23$ MHz, and saturation irradiance $I_S = \pi h c \Gamma/(3\lambda^3) \approx 180$ mW/cm². As shown in Fig. 3, the four hyperfine levels of N = 1 are all addressed with detuning within 2Γ to the respective peaks.

As for the undesired leak, the leakage decay to the intermediate electronic state $B^2\Sigma^+$ will end up going back to $|X, v = 0, N = 0, 2, +\rangle$ due to selection rules, and the microwave remixing method will be used to eliminate this leakage, similar to Refs. [23,46]. Microwave radiation tuned to $f_0 = \sim 13$ GHz can drive $|N = 0, F = 0\rangle \Leftrightarrow |N = 1, J = 3/2, F = 1\rangle$ and $|N = 0, F = 1\rangle \Leftrightarrow |N = 1, J = 3/2, F = 2\rangle$ transitions to mix the N = 0 and 1 hyperfine levels, while the N = 2is remixed to N = 1 just by doubling the frequency f_0 to drive $\Delta J = +1, \Delta F = +1$ transitions. The corresponding frequency values are listed in Table V.

IV. BRANCHING RATIOS FOR THE $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ TRANSITION

The distribution of the laser intensity can be determined by the branching ratios which reflect the transition strengths for all the hyperfine decay paths. In order to calculate the branching ratios, J mixing for the electric dipole transitions in $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ was considered first. The calculations were based on

$$|F = N^{\pm}, M\rangle = x^{\pm} |J = N + \frac{1}{2}, F = N, M\rangle$$

+ $y^{\pm} |J = N - \frac{1}{2}, F = N, M\rangle$, (7)



FIG. 3. The proposed sideband modulation scheme to simultaneously cover all four hyperfine levels of the $|X, v = 0, N = 1\rangle$ state. The calculated molecular fluorescence spectra (black curved line) are shown with their natural linewidths and central frequencies (solid black lines). The relative intensity represents the branching ratios from the $|C, v' = 0, J' = 1/2, +\rangle$ state to each hyperfine level. Two EOMs are used in the scheme with modulation frequency of $f_{mod1} = 395$ MHz (blue) and $f_{mod2} = 495$ MHz (red) [45].

TABLE VI. The *g* factors of the $X^2 \Sigma_{1/2}$ ($\upsilon = 0$) state.

Mixed label	Superposition of pure <i>J</i> states	g (without J mixing)	g (with J mixing)
$ J = 1/2, F = 0\rangle$	$ J = 1/2, F = 0\rangle$	0.00	0.00
$ J = 1/2, F = 1\rangle$	$0.8575 J = 1/2, F = 1\rangle - 0.5145 J = 3/2, F = 1\rangle$	-0.33	-0.44
$ J = 3/2, F = 1\rangle$	$0.5145 J = 1/2, F = 1\rangle + 0.8575 J = 3/2, F = 1\rangle$	0.83	0.94
$ J = 3/2, F = 2\rangle$	$ J=3/2, F=2\rangle$	0.50	0.50

and

$$\frac{x^{\pm}}{y^{\pm}} = -\frac{\langle J = N + \frac{1}{2}, F = N, M | H | J = N - \frac{1}{2}, F = N, M \rangle}{\langle J = N + \frac{1}{2}, F = N, M | H | J = N + \frac{1}{2}, F = N, M \rangle - E_N^{\pm}},$$
(8)

the details of which are described in Ref. [47]. Here x and y represent the coefficients of the superposition of pure J states. As shown in Table VI, J mixing exists only in F = 1 of the N = 1 manifold, and the g factors listed are only valid for magnetic field that induces small energy shift comparable to the hyperfine structure.

The calculation of the electric dipole transitions of $C^2 \Pi_{1/2} \leftarrow X^2 \Sigma_{1/2}$ is based on Hund's case (a) basis $|\Lambda, S, \Sigma, \Omega, J, I, F, M_F\rangle$. According to the equation

$$|\Lambda, N, S, J\rangle = \sum_{\Omega} \sum_{\Sigma} (-1)^{J+\Omega} \sqrt{2N+1} \begin{pmatrix} S & N & F \\ \Sigma & \Lambda & -\Omega \end{pmatrix} |\Lambda, S, \Sigma, \Omega, J, F\rangle,$$
(9)

the pure J states of the Hund's case (b) X state can be converted to the Hund's case (a) basis, and the Hund's case (a) C state can be expressed by

$$|\Lambda^{s}, J, M, \pm\rangle = \frac{1}{\sqrt{2}} (|\Lambda^{s}, S, \Sigma, J, \Omega, M\rangle \pm (-1)^{J-S} | -\Lambda^{s}, S, -\Sigma, J, -\Omega, M\rangle).$$
(10)

The electric dipole matrix elements were then calculated by

$$m_{ij} = \langle i|T^{(1)}(d)|j\rangle = \sum_{p=-1}^{1} (-1)^{F'-M'_F} \begin{pmatrix} F' & 1 & F \\ -M'_F & p & M_F \end{pmatrix} (-1)^{F+J'+I+1} \sqrt{(2F'+1)(2F+1)} \begin{cases} J & F & I \\ F' & J' & 1 \end{cases}$$
$$\times \sum_{q=-1}^{1} (-1)^{J'-\Omega'} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix} \sqrt{(2J'+1)(2J+1)} \times \langle \Lambda', S, \Sigma'|T_q^{(1)}(d)|\Lambda, S, \Sigma \rangle, \tag{11}$$

and $T^{(1)}(d)$ is the electric dipole operator written in the spherical tensor. More details are described in Ref. [48] [Eqs. (6.149) and (6.234)]. A similar method was also used for BaF [46] and MgF [49]. The branching ratios for decays from hyperfine sublevels in $|C, J = 1/2, +\rangle$ to hyperfine sublevels in $|X, N = 1, -\rangle$ are listed in Table VII.

V. INTERACTION OF THE EXTERNAL MAGNETIC FIELD WITH HYPERFINE LEVELS OF HgF

In order to study the features of the HgF magneto-optical trap (MOT), it is crucial to analyze the effects of the external magnetic field upon the HgF $X^2 \Sigma_{1/2}$ hyperfine levels. The Hamiltonian and matrix expression of the Zeeman interaction are given by

$$\hat{H}_{\text{Zeeman}} = g_s \mu_B T^1(\hat{S}) T^1_{p=0}(\hat{B}) + g_L \mu_L T^1(\hat{L}) T^1_{p=0}(\hat{B}) - g_I \mu_N T^1(\hat{I}) T^1_{p=0}(\hat{B}),$$
(12)

and

$$\langle N', S, J', I, F', M'_F | g_S \mu_B T^1(\hat{S}) T^1_{p=0}(\hat{B}) | N, S, J, I, F, M_F \rangle = \delta_{N'N} \delta_{M'_F M_F} g_S \mu_B B_Z (-1)^{F-M_F + F' + 2J + I + N + S} [(2J+1)(2J'+1)(2F+1)(2F'+1)]^{1/2} [S(S+1)(2S+1)]^{1/2} \times \begin{cases} J S N \\ S J' 1 \end{cases} \begin{cases} F J I \\ J' F' 1 \end{cases} \begin{pmatrix} F & 1 F' \\ -M_F & 0 M_F \end{pmatrix}.$$
(13)

For the Zeeman term of the $X^2 \Sigma_{1/2}$ state, $\Lambda = 0$, μ_B , and μ_N represent the Bohr magneton and nuclear magneton with $\mu_B/\mu_N = 1836$, while g_S, g_L , and g_I are the electron, electron orbital, and nuclear *g* factors with the values of 2.002,

1, and 5.585, respectively. To sum up, only the first term of Eq. (12) is significant. Thus, the matrix representation of Zeeman effect is expressed by Eq. (13), and we present the Zeeman shift of the $X^2 \Sigma_{1/2}$ (N = 1) state in Fig. 4.

TABLE VII. Calculated hyperfine branching ratios for decays from the $C^2 \Pi_{1/2}$ (J = 1/2, +) to $X^2 \Sigma_{1/2}$ (N = 1, -) state of HgF.

			F'=0		F' = 1	
J	F	M_F	$M'_F = 0$	$M'_F = -1$	$M'_F = 0$	$M'_{F} = 1$
3/2	2	-2	0.0000	0.1667	0.0000	0.0000
		-1	0.0000	0.0833	0.0833	0.0000
		0	0.0000	0.0278	0.1111	0.0278
		1	0.0000	0.0000	0.0833	0.0833
		2	0.0000	0.0000	0.0000	0.1667
3/2	1	-1	0.0019	0.1486	0.1486	0.0000
		0	0.0019	0.1486	0.0000	0.1486
		1	0.0019	0.0000	0.1486	0.1486
1/2	1	-1	0.3315	0.1014	0.1014	0.0000
		0	0.3315	0.1014	0.0000	0.1014
		1	0.3315	0.0000	0.1014	0.1014
1/2	0	0	0.0000	0.2222	0.2222	0.2222

As shown in Fig. 4, the magnetic sublevels of opposite M_F values for the same J and F will split as the magnetic field grows. The g factor of each hyperfine structure was then calculated by applying a rather small magnetic field and we adopted $g_F = \Delta U/(M_F \mu_B B)$, where B is the small magnetic

field and ΔU is the corresponding energy difference. For the MOT experiment, the typical magnetic field is about several gauss. For HgF, $|J = 3/2, F = 2\rangle$ and $|J = 3/2, F = 1\rangle$ states have positive *g* factors: $g_2 = 0.5$ and $g_1^+ = 0.94$, with "+" indicating the higher *J* state of the same *F*, and these states split symmetrically into eight magnetic sublevels. However, the *g* factor of $|J = 1/2, F = 1\rangle$ turned out to be -0.44 and the *g* factor of $|J = 1/2, F = 0\rangle$ is even close to zero. The hyperfine structure of the HgF $X^2 \Sigma_{1/2}$ (N = 1) state used in the MOT experiment satisfies the requirement of the type-II MOT system where $F' \leq F$ [50].

VI. SUITABILITY FOR eEDM PRECISION MEASUREMENT EXPERIMENT

For the *e*EDM measurement, the achievable statistical uncertainty can be expressed as $d_e = \hbar/(2E_{\rm eff}\tau\sqrt{NT})$, where \dot{N} is the detected rate of the molecules, *T* is the total integration time, and τ is the interaction time of the molecules with external fields in the Ramsey interferometer. $E_{\rm eff}$ is the internal effective electric field of the HgF $X^2 \Sigma_{1/2}$ state, which is closely related to the applied electric field $E_{\rm app}$ and its relevant polarization factor η . This polarization factor was calculated



FIG. 4. The Zeeman shift of $X^{2}\Sigma_{1/2}$ (N = 1): (a) for |J = 1/2, F = 0), (b) for |J = 1/2, F = 1), (c) for |J = 3/2, F = 1), and (d) for |J = 3/2, F = 2).



FIG. 5. Variation of E_{eff} with respect to E_{app} for the HgF $X^2 \Sigma_{1/2}$ state. If a normal operating electric field such as $E_{\text{app}} = 10 \text{ kV/cm}$ is chosen, the effective field E_{eff} turns out to be about 62 GV/cm.

from dividing the expectation value of Hamiltonian H_d by E_{app} . As shown in Fig. 5, if the applied electric field E_{app} is 10 kV/cm, the corresponding E_{eff} is 62 GV/cm, compared with YbF of 14.5 GV/cm and BaF of 9 GV/cm, respectively, under the same E_{app} .

In order to suppress the statistical uncertainty, the increase of \dot{N} can be realized by improving the molecular flux of the beam source, remixing the molecules of the other rotational states to the desired probing state before the interferometry measurement. The decrease of the forward velocity of the molecular species can effectively increase the interaction time. For the ²⁰²Hg¹⁹F radical, a single photon at 256 nm could result in a recoil velocity of ~7 mm/s, and the molecular beam exiting from a two-stage buffer gas cooling source can be depicted with a forward velocity of about 75 m/s [51]. Our calculations show that only ~9 × 10³ photons should be scattered so as to slow the molecules down to ~10 m/s, which is the capture velocity of a three-dimensional (3D) MOT. In principle, up to ~10⁵ photons can be scattered if the fourth laser beam is added.

With the development of MOT and optical molasses methods, SrF [52], CaF [53,54], and YO [55] with up to $\sim 1 \times 10^5$

- [1] E. M. Purcell and N. F. Ramsey, Phys. Rev. 78, 807 (1950).
- [2] N. Fortson, P. Sandars, and S. Barr, Phys. Today 56(6), 33 (2003).
- [3] J. J. Hudson, D. M. Kara, I. J. Smallman, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Nature (London) 473, 493 (2011).
- [4] J. Baron et al. (The ACME Collaboration), Science 343, 269 (2014).
- [5] W. B. Cairncross, D. N. Gresh, M. Grau, K. C. Cossel, T. S. Roussy, Y. Ni, Y. Zhou, J. Ye, and E. A. Cornell, Phys. Rev. Lett. **119**, 153001 (2017).
- [6] V. Andreev *et al.* (The ACME Collaboration), Nature (London) 562, 355 (2018).
- [7] Y. Nir, CP Violation in and Beyond the Standard Model, in Proceedings of the 27th SLAC Summer Institute on Particle Physics (SSI '99), Stanford, USA, July 7–16, 1999, The

molecules have been loaded into a 3D MOT. For the *e*EDM measurement, the most sensitive experiments can be conducted with trapped cold molecules, and up to 2 s of trap lifetime has been obtained in the trap experiments [56,57]. We can therefore propose that the HgF radicals can survive in the trap with the interaction time of 1 s and $\sim 1 \times 10^5$ molecules are trapped with a repetition rate of 1 Hz for the beam source, considering the published experimental results. With all the parameters mentioned above, the corresponding statistical uncertainty is estimated to be $\sim 6 \times 10^{-32} e \text{ cm/day}^{1/2}$. In order to achieve sensitivity at this statistical limit, the noise due to random fluctuations of the magnetic field must be suppressed to fT Hz^{-1/2} level [58], which can be achieved by good magnetic shielding together with the use of appropriate materials inside the apparatus [58].

VII. CONCLUSION

In this paper, we have theoretically investigated the electronic, rovibrational, and hyperfine structures of 202 Hg¹⁹F and verified the highly diagonal Franck-Condon factors of the main transitions by the RKR method and Morse approximation. We also studied the Zeeman shift and hyperfine structure magnetic g factors of its $X^2 \Sigma_{1/2}$ (N = 1) state with the effective Hamiltonian approach. Our paper indicates that the HgF radical can be a promising candidate for laser cooling; with less than 1×10^4 photons to be scattered, the HgF radical can be longitudinally slowed from 75 to 10 m/s. The statistical sensitivity of the *e*EDM measurement is estimated to be about $6 \times 10^{-32} e$ cm in the trap, indicating that the laser-cooled 202 Hg¹⁹F radical might be a competitive *e*EDM candidate when compared with the most recent ThO result of $d_e = (4.3 \pm 3.1_{stat} \pm 2.6_{syst}) \times 10^{-30} e$ cm.

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ICTP Series in Theoretical Physics (World Scientific, 1999), pp. 165–243.

- [8] J. M. Pendlebury and E. A. Hinds, Nucl. Instrum. Methods Phys. Res. A 440, 471 (2000).
- [9] S. Eckel, P. Hamilton, E. Kirilov, H. W. Smith, and D. DeMille, Phys. Rev. A 87, 052130 (2013).
- [10] N. E. Shafer-Ray, Phys. Rev. A 73, 034102 (2006).
- [11] J. Lee, J. Chen, L. V. Skripnikov, A. N. Petrov, A. V. Titov, N. S. Mosyagin, and A. E. Leanhardt, Phys. Rev. A 87, 022516 (2013).
- [12] A. D. Kudashov, A. N. Petrov, L. V. Skripnikov, N. S. Mosyagin, T. A. Isaev, R. Berger, and A. V. Titov, Phys. Rev. A 90, 052513 (2014).
- [13] V. S. Prasannaa, A. C. Vutha, M. Abe, and B. P. Das, Phys. Rev. Lett. 114, 183001 (2015).

- [14] D. N. Gresh, K. C. Cossel, Y. Zhou, J. Ye, and E. A. Cornell, J. Mol. Spectrosc. **319**, 1 (2016).
- [15] P. Aggarwal et al., Eur. Phys. J. D, 72, 197 (2018).
- [16] J. Lim, J. R. Almond, M. A. Trigatzis, J. A. Devlin, N. J. Fitch, B. E. Sauer, M. R. Tarbutt, and E. A. Hinds, Phys. Rev. Lett. 120, 123201 (2018).
- [17] T. A. Isaev, S. Hoekstra, and R. Berger, Phys. Rev. A 82, 052521 (2010).
- [18] L. Xu, B. Wei, Y. Xia, L. Z. Deng, and J. P. Yin, Chin. Phys. B 26, 033702 (2017).
- [19] L. V. Skripnikov, A. N. Petrov, and A. V. Titov, J. Chem. Phys. 139, 221103 (2013).
- [20] M. G. Kozlov, J. Phys. B 30, L607 (1997).
- [21] A. N. Petrov, N. S. Mosyagin, T. A. Isaev, and A. V. Titov, Phys. Rev. A 76, 030501(R) (2007).
- [22] S. Elmoussaoui, W. Chmaisani, and M. Korek, J. Quant. Spectrosc. Radiat. Transfer 201, 64 (2017).
- [23] M. Yeo, M. T. Hummon, A. L. Collopy, B. Yan, B. Hemmerling,
 E. Chae, J. M. Doyle, and J. Ye, Phys. Rev. Lett. 114, 223003 (2015).
- [24] H. Hachisu, K. Miyagishi, S. G. Porsev, A. Derevianko, V. D. Ovsiannikov, V. G. Palchikov, M. Takamoto, and H. Katori, Phys. Rev. Lett. **100**, 053001 (2008).
- [25] B. Graner, Y. Chen, E. G. Lindahl, and B. R. Heckel, Phys. Rev. Lett. 116, 161601 (2016).
- [26] H. G. Howell, Proc. R. Soc. London A 182, 95 (1943).
- [27] T. Dreiling and D. Setser, J. Chem. Phys. 86, 2276 (1982).
- [28] T. Dreiling and D. Setser, J. Chem. Phys. **79**, 5423 (1983).
- [29] L. B. Knight, Jr., T. A. Fisher, and M. B. Wise, J. Chem. Phys. 74, 6009 (1981).
- [30] I. Lakoba, Sov. J. Quantum Electron 18, 1121 (1988).
- [31] T. D. Dreiling, D. W. Setser, and S. Ferrero, J. Chem. Soc. Faraday Trans. 278, 1311 (1982).
- [32] E. A. Hinds and K. Sangster, Testing Time Reversal Sym metry with Molecules, in *Proceedings of Time Reversal-The Arthur Rich Memorial Symposium, Ann Arbor, Michigan, 1991*, edited by M. Skalsey, P. H. Bucksbaum, R. S. Conti, and D. W. Gidley, AIP Conf. Proc. No. 270 (AIP, New York, 1993), p. 77.
- [33] D. Egorov, W. Campbell, B. Friedrich, S. Maxwell, E. Tsikata, L. Van Buuren, and J. Doyle, Eur. Phys. J. D 31, 307 (2004).
- [34] K. P. Giapis, T. A. Moore, and T. K. Minton, J. Vac. Sci. Technol. A 13, 959 (1995).
- [35] R. J. Levis, C. J. Waltman, L. M. Cousins, R. G. Copeland, and S. R. Leone, J. Vac. Sci. Technol. A 8, 3118 (1990).
- [36] G. Dharmasena, K. Copeland, J. H. Young, R. A. Lasell, T. R. Phillips, G. A. Parker, and M. Keil, J. Phys. Chem. A 101, 6429 (1997).

- [37] M. Faubel, B. Martinez-Haya, L. Y. Rusin, U. Tappe, and J. Toennies, J. Phys. D 29, 1885 (1996).
- [38] P. Sivakumar, C. P. McRaven, P. M. Rupasinghe, T. Z. Yang, N. E. Shafer-Ray, T. J. Sears, and G. E. Hall, Mol. Phys. 108, 927 (2010).
- [39] A. L. G. Rees, Proc. Phys. Soc. 59, 998 (1947).
- [40] A. Frank, A. L. Rivera, and K. B. Wolf, Phys. Rev. A 61, 054102 (2000).
- [41] R. Zhao, X. Fu, L. Zhang, S. Fang, J. Sun, Y. Feng, Z. Xu, and Y. Wang, Appl. Opt. 56, 8973 (2017).
- [42] R. A. Frosch and H. M. Foley, Phys. Rev. 88, 1337 (1952).
- [43] M. G. Kozlov, L. N. Labzovskii, and A. O. Mitrushchenkov, Zh. Eskp. Teor. Fiz. **100**, 749 (1991) [Sov. Phys. JETP **73**, 415 (1991)].
- [44] M. Kozlov and L. Labzowsky, J. Phys. B 28, 1933 (1995).
- [45] An inquiry about the features of the EOM indicate that EOMs of the 395- and 495-MHz modulating frequency are commercially available from the Qubig company.
- [46] T. Chen, W. H. Bu, and B. Yan, Phys. Rev. A 94, 063415 (2016).
- [47] B. E. Sauer, Jun Wang, and E. A. Hinds, J. Chem. Phys. 105, 7412 (1996).
- [48] J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge University, Cambridge, England, 2003).
- [49] X. Yang, C. Li, Y. Yin, S. Xu, X. Li, Y. Xia, and J. Yin, J. Phys. B 50, 015001 (2017).
- [50] M. R. Tarbutt, New J. Phys. 17, 015007 (2015).
- [51] H.-I. Lu, J. Rasmussen, M. J. Wright, D. Patterson, and J. M. Doyle, Phys. Chem. Chem. Phys. 13, 18986 (2011).
- [52] J. F. Barry, D. J. McCarron, E. B. Norrgard, M. H. Steinecker, and D. DeMille, Nature (London) 512, 286 (2014).
- [53] L. Anderegg, B. L. Augenbraun, E. Chae, B. Hemmerling, N. R. Hutzler, A. Ravi, A. Collopy, J. Ye, W. Ketterle, and J. M. Doyle, Phys. Rev. Lett. **119**, 103201 (2017).
- [54] S. Truppe, H. J. Williams, M. Hambach, L. Caldwell, N. J. Fitch, E. A. Hinds, B. E. Sauer, and M. R. Tarbutt, Nat. Phys. 13, 1173 (2017).
- [55] A. L. Collopy, S. Ding, Y. Wu, I. A. Finneran, L. Anderegg, B. L. Augenbraun, J. M. Doyle, and J. Ye, Phys. Rev. Lett. 121, 213201 (2018).
- [56] D. J. McCarron, M. H. Steinecker, Y. Zhu, and D. DeMille, Phys. Rev. Lett. **121**, 013202 (2018).
- [57] H. J. Williams, L. Caldwell, N. J. Fitch, S. Truppe, J. Rodewald, E. A. Hinds, B. E. Sauer, and M. R. Tarbutt, Phys. Rev. Lett. 120, 163201 (2018).
- [58] M. R. Tarbutt, B. E. Sauer, J. J. Hudson, and E. A. Hinds, New J. Phys. 15, 053034 (2013).