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Theoretical study of low-lying electronic terms and transition moments for HfF$^+$ for the electron electric-dipole-moment search

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We report *ab initio* relativistic 20-electron correlation calculations of electric-dipole transition moments for nine low-lying electronic states of HfF$^+$, which it is suggested to be used in experiments to search for the electric-dipole moment of the electron. Radiative lifetimes for the lowest vibrational levels of the first excited $^3\Delta_1$ electronic state are calculated and its population scheme is suggested. The influence of correlation of the 4f electrons of Hf is studied.

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I. INTRODUCTION

The search for the electric-dipole moment (EDM) of the electron (d_e or eEDM below) remains one of the most fundamental problems in physics. Only upper limits for $|d_e|$ were obtained up to now. The tightest bound on d_e was given in the experiment on the atomic Tl beam [1], which established $|d_e|<1.6\times 10^{-27}e$ cm (e is the charge of the electron). Molecular systems provide a way to get significantly enhanced sensitivity, since the effective intramolecular electric field acting on electrons in polar molecules can be five or more orders of magnitude higher than the field available in the laboratory [2–4].

It is expected that the new generation of the eEDM experiments employing polar heavy-atom molecules can reach sensitivity of 10^{-30}–$10^{-28}e$ cm$/\sqrt{\text{day}}$ (e.g., see [5]). Thus, their results will influence deeply all the popular extensions of the Standard model, in particular supersymmetry, even if bounds on the P,T-odd effects compatible with zero are obtained (see [6,7] and references therein). New ways of searching for the eEDM with trapped cold molecular cations were investigated during the last years by Cornell and coworkers. The encouraging progress was recently achieved by his group in producing and studying the electronic-vibrational spectra of the HfF$^+$ cation. Theoretical investigation of the required properties for HfF$^+$ (spectroscopic constants for 10 low-lying electronic states, hyperfine structure, and the effective electric field E_{eff} acting on an electron in the $^3\Delta_1$ state) was performed in our paper [8]. We note that the calculated energy for the $^1\Sigma^+\rightarrow{}^3\Pi_1$ transition is in good agreement with the pilot experimental datum by the Cornell group [9]. It was shown in [8] that the $^3\Delta_1$ state has large E_{eff}=5.84×10^{24} Hz$/e$ cm. Unfortunately, it was obtained that $^3\Delta_1$ is not the ground state, but its radiative lifetime was estimated as 0.5 s. This lifetime is sufficient for the experiment. The $^3\Delta_1$ state was calculated to be lying about only 0.2 eV higher than the $^1\Sigma^+$ ground state. However, the 4f electrons of Hf were not correlated in [8]. We show in the present paper that accounting for correlation of the 4f electrons do not exert dramatic influence on the transition energy of interest and even on the lifetime (5) of the $^3\Delta_1$ (despite the lifetime is proportional to the third power of the transition energy and absolute value of the latter is small). The more accurate data for the transition dipole moment $^1\Sigma^+\rightarrow{}^3\Delta_1$ and, consequently, more reliable values for the radiative lifetimes of the lowest vibrational levels of the $^3\Delta_1$ state are also presented. Besides, the data for other transition dipole moments are calculated. These data are used to study possible schemes of populating the excited $^3\Delta_1$ state by the laser beam. In the following section we give more detail discussion of the used methods than it was done in our rapid communication [8].

II. METHODS AND CALCULATIONS

A. GRECP method

When core electrons of a heavy-atom molecule do not play an active role (i.e., their relaxation in the molecule is negligible) the effective Hamiltonian with relativistic effective core potential (RECP) can be presented in the form

$$\mathbf{H}^{Ef}=\sum_{i_v}[\mathbf{h}^{\text{Schr}}(i_v)+\mathbf{U}^{Ef}(i_v)]+\sum_{i_v>j_v}\frac{1}{r_{i_vj_v}}. \tag{1}$$

Hamiltonian (1) is written only for a valence subspace of electrons, which are treated explicitly and denoted by indices i_v and j_v. In practice, this subspace is often extended by inclusion of some outer core shells for better accuracy. In Eq. (1), $\mathbf{h}^{\text{Schr}}$ is the one-electron Schrödinger Hamiltonian

$$\mathbf{h}^{\text{Schr}}=-\frac{1}{2}\vec{\nabla}^2-\frac{Z_{ic}}{r}, \tag{2}$$

where Z_{ic} is the charge of the nucleus decreased by the number of inner core electrons. $\mathbf{U}^{Ef}$ is an RECP [or relativistic pseudopotential (PP)] operator that can be written in the separable (e.g., see Ref. [10] and references therein) or radially local (semilocal) [11] approximations when the valence pseudospinors are smoothed in heavy-atom cores. This smoothing allows one to reduce the number of primitive Gaussian basis functions required for appropriate description of valence spinors in subsequent molecular calculations and also to exclude the small components of the four-component

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Dirac spinors from the RECP calculations, with relativistic effects being taken into account by j-dependent effective potentials. Contrary to the four-component wave function used in Dirac-Coulomb(-Breit) calculations, the pseudo-wave function in the RECP case can be both two and one component.

Besides, the generalized RECP (GRECP) operator [12,13] can be used in Eq. (1) that includes the radially local, separable and Huzinaga-type [14] relativistic PPs as its components and some special cases. The GRECP concept was introduced and developed in a series of papers (see Refs. [12,13,15–18] and references therein). In contrast to other RECP methods, GRECP employs the idea of separating the space around a heavy atom into three regions: Inner core, outer core, and valence, which are treated differently. It allows one to attain theoretically any desired accuracy, while requiring moderate computational efforts since the overall accuracy is limited in practice by possibilities of correlation methods.

Two of the major features of the GRECP version with the separable correction described here are generating of the effective potential components for the pseudospinors which may have nodes, and addition of nonlocal separable terms with projectors on the outer core pseudospinors to the conventional semilocal RECP operator. The problem of division by zero appearing in the cases of pseudospinors with nodes is overcome in the GRECP method by interpolating the corresponding potentials in the vicinity of these nodes [19,20]. It was shown both theoretically and computationally that the interpolation errors are small enough. That allows us to generate different potentials for the cases of outer core and valence pseudospinors with the same quantum numbers l and j, unlike the conventional RECP approach. In turn, the nonlocal separable terms in the GRECP operator account for difference between these potentials, which in the outer region is defined by smoothing within the inner core as is shown in Refs. [21–23] and in many cases this difference cannot be neglected for "chemical accuracy" (about 1 kcal/mol or 350 cm^{-1}) of valence energies. The more circumstantial description of distinctive features of the GRECP as compared to the original RECP schemes is given in Refs. [24,25]. Some other GRECP versions are described and discussed in details in Refs. [12,13,17].

The GRECP operator in the spinor representation [12,26] is naturally used in atomic calculations. The spin-orbit representation of this operator which can be found in Refs. [12,27] is more efficient in practice being applied to calculation of molecules. Despite the complexity of the expression for the GRECP operator, the calculation of its one-electron integrals is not notably more expensive than that for the case of the conventional radially local RECP operator.

The GRECP simulating interaction of 12 outer core and valence electrons of Hf with the explicitly excluded $1s$ to $4f$ electrons (60 inner core electrons) is used in 20-electron calculations of HfF^{+}.

B. Freezing the innermost shells from the outer core space

The "freezing" of innermost shells from the outer core space of electrons within the "small core" GRECPs is sometimes required because the accuracy of the GRECPs generated directly for a given number of explicitly treated electrons cannot always correspond to the accuracy of the conventional "frozen core" approximation with the same space of explicitly treated electrons (without accounting for the frozen states). That space is usually chosen as a minimal one required for attaining a given accuracy. It was noted in Refs. [20,26] that using essentially different smoothing radii for spinors with different lj is not expedient since the (G)RECPs errors are mainly accumulated by the outermost from them. In turn, explicit treatment of all of the outer core shells of an atom with the same principal quantum number is not usually reasonable in molecular (G)RECP calculations because of essential increase in computational efforts without serious improvement of accuracy. A natural way out is to "freeze" the innermost of them before performing molecular calculation but this cannot be done directly if the spin-orbit molecular basis set is used whereas the core shells should be better frozen as spinors.

In order to exclude ("freeze") explicitly those innermost shells (denoted by indices f below) from molecular (G)RECP calculation without changing the radial node structure of other (outermore core and valence) shells in the core region, the energy level shift technique can be applied to overcome the above contradiction [12,28]. Following Huzinaga *et al.* [14], one should add the effective core operator $\mathbf{U}^{Ef}_{\mathrm{Huz}}$ containing the Hartree-Fock field operators, the Coulomb ($\tilde{\mathbf{J}}$) and spin-dependent exchange ($\tilde{\mathbf{K}}$) terms, over these core spinors together with the level shift terms to the one-electron part of the Hamiltonian (1):

$$\mathbf{U}^{Ef}_{\mathrm{Huz}} = (\tilde{\mathbf{J}} - \tilde{\mathbf{K}})[\tilde{f}_{n_f lj}] + \sum_{n_f,l,j} B_{n_f lj} |\tilde{f}_{n_f lj}\rangle\langle\tilde{f}_{n_f lj}| \tag{3}$$

(i.e., $\varepsilon_{n_f lj} \to \varepsilon_{n_f lj} + B_{n_f lj}$), where $|\tilde{f}_{n_f lj}\rangle\langle\tilde{f}_{n_f lj}|$ are the projectors on the core spinors $\tilde{f}_{n_f lj}$ and $\varepsilon_{n_f lj}$ are their one-electron energies. The $B_{n_f lj}$ parameters are presented as $M|\varepsilon_{n_f lj}|$ in our codes and $M > 1$ to prevent occupying the corresponding states in calculations; it is usually selected as $M \gg 1$ in our studies. Such nonlocal terms are needed in order to prevent collapse of the valence electrons to the frozen core states. They introduce some "soft orthogonality constraint" between the "frozen" and other explicitly treated outermore core and valence electronic states.

All the terms with the frozen core spinors (the level shift operator and exchange interactions) can be transformed to the spin-orbit representation in addition to the spin-independent Coulomb term, using the identities for the $\mathbf{P}_{lj}$ projectors [29],

$$\mathbf{P}_{l,j=l\pm 1/2} = \frac{1}{2l+1}\left[\left(l + \frac{1}{2} \pm \frac{1}{2}\right)\mathbf{P}_l \pm 2\mathbf{P}_l \vec{\mathbf{l}} \cdot \vec{\mathbf{s}} \mathbf{P}_l\right],$$

$$\mathbf{P}_{lj} = \sum_{m_j=-j}^{j} |ljm_j\rangle\langle ljm_j|,$$

$$\mathbf{P}_l = \sum_{m_l=-l}^{l} |lm_l\rangle\langle lm_l|. \tag{4}$$

where $\vec{\mathbf{l}}$ and $\vec{\mathbf{s}}$ are operators of the orbital and spin momenta, $|ljm_j\rangle\langle ljm_j|$ is the projector on the two-component spin-angular function χ_{ljm_j}, $|lm_l\rangle\langle lm_l|$ is the projector on the spherical function Y_{lm_l}.

More importantly, these outer core pseudospinors can be frozen in calculations with the spin-orbit basis sets and they can already be frozen at the stage of calculation of the one-electron matrix elements of the Hamiltonian, as implemented in the MOLGEP code [30]. Thus, any integrals with indices of the frozen spinors are completely excluded after the integral calculation step. The multiplier $M=30$ was chosen in the present molecular calculations to prevent mixing the shifted core states to the wave function due to correlations but not to get poor reference wave function in the initial spin-averaged calculations at the same time (as would be for $M\to\infty$).

In fact, the combined GRECP version, with separable and Huzinaga-type terms, is a new pseudopotential treating some minimal number of electrons explicitly but which already provide the accuracy approaching to that of the frozen core approximation. The efficiency of using the "freezing" procedure within the GRECP method was first studied in calculations of Tl [12] and TlH [28].

In 10-electron calculations, which are substantially less time consuming, $5s$ and $5p$ spinors of hafnium and $1s$ orbital of fluorine are frozen from the states averaged over the nonrelativistic configurations $5d^2 6s^{0.6} 6p^{0.4}$ for Hf$^+$ and $2s^2 2p^5$ for F, and not treated explicitly.

C. SODCI method

The spin-orbit direct configuration interaction (SODCI) method is well described in papers [31,32]. In the current version of the method, calculations are carried out in the ΛS basis set of many-electron spin-adapted (and space symmetry-adapted) functions (SAFs). The different ΛS sets of SAFs are collected together in accord to the relativistic double-group symmetry requirements for the final configuration interaction (CI) calculation. In the present study of the molecule having the ${}^{2S'+1}\Lambda'$ leading term, configurations from all the symmetry allowed ΛS sets with $S\leqslant 2$ are included into calculations.

All the possible singly and doubly excited configurations with respect to some reference configurations are generated (see below for choice of the reference configurations). A generated configuration is included in the final CI space if its addition to the reference set leads to lowering in the total energy by the value more than some threshold T. This lowering is estimated with the help of the A_k version of perturbation theory [33], in which the correlation and spin-orbit interaction are considered as perturbations and the wave function (obtained from the CI calculation in the space of the reference configurations for all the ΛS irreducible representations) is taken as a zero approximation (see [28,34] for details). The lowerings in the total energies for the unselected configurations are employed for the $T=0$ threshold extrapolation. The generalized multireference analogue [35] of the Davidson correction [36] (full CI correction) is also calculated.

In the present calculations, those configurations are chosen as the reference (main) configurations which give the largest contribution to the wave function (i.e., have the largest square of the absolute value of the CI coefficient (C_I), and thus, that $C^2_{\mathrm{ref}} \equiv \Sigma_{I\in \mathrm{ref}} |C_I|^2 = C$, where $C=0.973$ for 10-electron and $C=0.942$ for 20-electron calculations. The configurations are obtained from results of the preliminary SODCI calculations in the relativistic double-group symmetry with the large threshold T. New SODCI calculation is then carried out with the smaller thresholds. The C is taken the same for each point on the potential curve [37]. Davidson and other corrections estimating contributions for higher than double excitations have an essential dependence on C^2_{ref}. The above selection criterion allows one to stabilize these corrections for different internuclear distances. This is important because the reliability of those corrections has a significant dependence on these values.

D. Basis sets and property calculations

The generalized correlation atomic basis set [38,39] $(12s16p16d10f10g)/[6s5p5d3f1g]$ is constructed for Hf. The ANO-L $(14s9p4d3f)/[4s3p2d1f]$ atomic basis set listed in the MOLCAS 4.1 library [40] was used for fluorine. The molecular orbitals are obtained by the complete active space self-consistent-field (CASSCF) method [40,41] with the spin-averaged part of the GRECP [12], i.e., only scalar-relativistic effects are taken into account at this stage. In the

TABLE I. The 10-electron SODCI calculations of transition dipole moments and molecule-frame electric-dipole moments for ${}^3\Delta_1$ state with respect to the center of mass. Axis z is directed from Hf to F. All values in a.u.

R	3.1	3.3	3.4	3.5	3.7	4.0
$D(R)_{{}^3\Delta_1\to{}^3\Delta_1}$	−1.15	−1.40	−1.52	−1.64	−1.87	−2.20
$D(R)_{{}^1\Sigma^+\to{}^3\Delta_1}$ (units of 10^{-2})	1.60	1.59	1.60	1.56	1.50	1.14
$D(R)_{{}^1\Sigma^+\to{}^3\Pi_1}$ (units of 10^{-1})	3.12	2.94	2.84	2.77	2.69	2.70
$D(R)_{{}^1\Sigma^+\to{}^1\Pi_1}$ (units of 10^{-1})	7.55	6.52	6.02	5.59	4.93	4.11
$D(R)_{{}^3\Delta_1\to{}^3\Pi_1}$ (units of 10^{-2})	3.78	4.00	4.13	4.25	4.51	4.99
$D(R)_{{}^3\Delta_1\to{}^1\Pi_1}$ (units of 10^{-2})	3.34	3.90	3.87	3.93	4.09	4.50
$D(R)_{{}^3\Delta_1\to{}^3\Pi_{0+}}$ (units of 10^{-1})	3.86	3.30	3.01	2.80	2.45	2.13

TABLE II. Transition and molecule-frame electric-dipole moments (with respect to the center of mass for $R=3.4$ a.u.) obtained in 20-electron calculations. Axis z is directed from Hf to F. All values in a.u.

	$^1\Sigma^+$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_3$	$^1\Delta_2$	$^3\Pi_{0+}$	$^3\Pi_1$	$^3\Pi_2$	$^1\Pi_1$
$^1\Sigma^+$	-1.20	1.95×10^{-2}	0	0	0	7.77×10^{-2}	3.55×10^{-1}	0	5.33×10^{-1}
$^3\Delta_1$		-1.50	1.35×10^{-2}	0	8.74×10^{-3}	3.30×10^{-1}	2.56×10^{-2}	8.42×10^{-3}	8.23×10^{-4}
$^3\Delta_2$			-1.48	1.93×10^{-2}	3.17×10^{-2}	0	2.31×10^{-1}	-2.10×10^{-2}	2.15×10^{-1}
$^3\Delta_3$				-1.49	4.69×10^{-2}	0	0	0.295	0
$^1\Delta_2$					-1.30	0	1.73×10^{-1}	4.17×10^{-2}	2.14×10^{-2}
$^3\Pi_{0+}$						-9.48×10^{-1}	8.42×10^{-3}	0	1.82×10^{-3}
$^3\Pi_1$							-1.05	2.95×10^{-2}	1.35×10^{-1}
$^3\Pi_2$								-1.02	-5.79×10^{-2}
$^1\Pi_1$									-1.24

CASSCF method, orbitals are subdivided into three groups: Inactive, active, and virtual. Inactive orbitals are doubly occupied in all the configurations; all possible occupations are allowed for active orbitals, whereas virtual orbitals are not occupied. So the wave function is constructed as a full configuration-interaction expansion in the space of active orbitals, and both active and inactive orbitals are optimized for subsequent correlation calculations of HfF$^+$. According to the C_{2v} point group classification scheme used in our codes, five orbitals in A_1, four in B_1 and B_2, and two in A_2 irreducible representations (irreps) are included in the active space. In 10-electron calculations, one orbital in the A_1 irrep (which is mainly the $2s$ orbital of F) belongs to the inactive space. In 20-electron CASSCF calculations, the $5s$ and $5p$ orbitals of Hf and $1s$ orbital of F are added to the space of inactive orbitals.

The 10 lowest states with the leading configurations $[\cdots]\sigma_1^2\sigma_2^2$ ($^1\Sigma^+$), $[\cdots]\sigma_1^2\sigma_2^1\delta^1$ ($^3\Delta_{1,2,3}$; $^1\Delta$), $[\cdots]\sigma_1^2\sigma_2^1\pi^1$ ($^3\Pi_{0^-,0^+,1,2}$; $^1\Pi$) were calculated. Here the σ_1 orbital is mainly formed by the $2p_z$ orbital of F with admixture of the $6p_z$ and $6s$ orbitals of Hf, σ_2 is mainly the $6s$ orbital of Hf with admixture of the $6p_z$ orbital of Hf, δ and π are mainly the $5d$ orbitals of Hf.

To obtain the spectroscopic parameters, six points listed in Table I and a point at 100 a.u. on the HfF$^+$ potential curves were calculated for 10 lowest-lying states in 10-electron calculations and for four states in 20-electron ones. The 20-electron calculation is substantially more time consuming; therefore the remaining six states were calculated for only one point, 3.4 a.u., in the present study. Comparing the latter calculations with corresponding 10-electron ones, the core ($5s^2$ and $5p^6$ shells of Hf and $1s^2$ shell of F) relaxation and correlation corrections to the T_e values, called "core corrections" below and in Table III, were estimated. Only the electronic $^1\Sigma^+$ state is below the $^3\Delta_1$ one. The radiative lifetime of the lowest vibrational levels of the latter with respect to its

TABLE III. Calculated spectroscopic parameters for HfF$^+$.

State	R_e (Å)	T_e (cm^{-1})	T_e with core correction[a]	w_e (cm^{-1})	D_e (cm^{-1})
		10-electron calculation			
$^1\Sigma^+$	1.784	0	0	751	51107
$^3\Delta_1$	1.810	866	1599	718	
$^3\Delta_2$	1.809	1821	2807	719	
$^3\Delta_3$	1.807	3201	4324	721	
$^1\Delta_2$	1.814	9246	11519	696	
$^3\Pi_{0-}$	1.856	9466	11910	689	
$^3\Pi_{0+}$	1.854	9753	12196	699	
$^3\Pi_1$	1.860	10190	12686	687	
$^3\Pi_2$	1.856	11898	14438	703	
$^1\Pi_1$	1.870	12642	14784	679	
		20-electron calculation			
$^1\Sigma^+$	1.781	0		790	51685
$^3\Delta_1$	1.806	1633		746	
$^3\Delta_2$	1.805	2828		748	
$^3\Delta_3$	1.804	4273		749	

[a] See Sec. II for details.

decay to the vibrational levels of the $^1\Sigma^+$ state can be written (here we are neglecting the rotational structure of the considered states) as

$$\tau^{-1}_{\mathrm{el}(^3\Delta_1,v2)} = \frac{4}{3c^3}\sum_{v1(\Delta E>0)} \Delta E^3 |\langle \Psi_{^3\Delta_1,v2}|\mathbf{d}|\Psi_{^1\Sigma^+,v1}\rangle|^2, \qquad (5)$$

where $\Delta E=(E_{(^3\Delta_1,v2)}-E_{(^1\Sigma^+,v1)})$ is the difference in the energies of the electronic-vibrational states $\Psi_{^3\Delta_1,v2}$ and $\Psi_{^1\Sigma^+,v1}$; $\mathbf{d}$ is the dipole moment operator. In the adiabatic approximation

$$|\langle \Psi_{^3\Delta_1,v2}|\mathbf{d}|\Psi_{^1\Sigma^+,v1}\rangle|^2 = |\langle \mathcal{X}_{^3\Delta_1,v2}(R) \times |D(R)_{^1\Sigma^+\rightarrow{}^3\Delta_1}|\mathcal{X}_{^1\Sigma^+,v1}(R)\rangle|^2, \qquad (6)$$

where $\mathcal{X}_{^3\Delta_1,v2}(R)$ is the vibrational wave function of the given electronic state and $D(R)_{^1\Sigma^+\rightarrow{}^3\Delta_1}$ is the electronic transition dipole moment as a function of the internuclear distance. The excited vibrational levels of the $^3\Delta_1$ state can also decay to the lower vibrational levels of the same, $^3\Delta_1$, electronic state. The radiative lifetime τ_{vibr} of this process is determined by the equations similar to (5) and (6) with replacing $^1\Sigma^+$ by $^3\Delta_1$. $D(R)_{^3\Delta_1\rightarrow{}^3\Delta_1}$ here is the total molecule-frame electric dipole moments for $^3\Delta_1$ state of the cation, calculated with respect to the center of mass. In Table I we tabulated $D^{10e}(R)$ for six points using the electronic wave functions obtained in the 10-electron calculations. In Table II we listed $D^{20e}(R)$ for point 3.4 a.u. using the electronic wave functions obtained in the 20-electron calculations. To calculate the radiative lifetimes according to Eqs. (5) and (6) we first use the $D^{10e}(R)$ values and then multiply the obtained τ_{el} and τ_{vibr} on the corresponding correction factors $[D^{10e}(3.4)/D^{20e}(3.4)]^2$. The vibrational wave functions $\mathcal{X}_{^3\Delta_1,v2}(R)$, $\mathcal{X}_{^1\Sigma^+,v1}(R)$ and electronic-vibrational energies were evaluated on the basis of the 20-electron SODCI calculations.

III. RESULTS AND DISCUSSION

The spectroscopic parameters for HfF$^+$ calculated in [8] and presented in Table III are the following: R_e is the equilibrium internuclear distance, D_e is the dissociation energy, T_e is the electronic excitation energy (calculated between the minima of the potential curves), w_e is the first coefficient in the power series for the vibrational energy $G=w_e v(v+1) - w_e x_e v^2(v+1)^2+\cdots$. The corresponding potential energy curves of HfF$^+$ are shown in Fig. 1. The potential energy curves are taken from 10-electron calculations but shifted (on the energy axis) to fit the D_e value obtained in the 20-electron calculations and T_e values obtained with 20-electron correction at point $R=3.4$ a.u. The discussion of this data can be found in [8]. As it is noted in the introduction, accounting for correlation of the $4f^{14}$ shell would be important but it is too time consuming computationally in molecular calculations. Here we estimate it in the atomic calculations. The results of the all-electron Fock space relativistic coupled cluster (RCC) [42] calculations for the transition from the terms of the $5d^16s^1$ configuration to the $5d^06s^2$ configuration are presented in Table IV. Three series of RCC calculations are performed: The $5s,5p$ shells are correlated in the 10-electron calculation; the $4f$ shells are correlated in the 16-electron calculation; the $4f,5s,5p$ shells are correlated in the 24-electron calculation additionally to the $5d,6s,6p$ ones. So the difference between the 24-electron and 16-electron calculations gives us the correlation contribution of the $5s,5p$

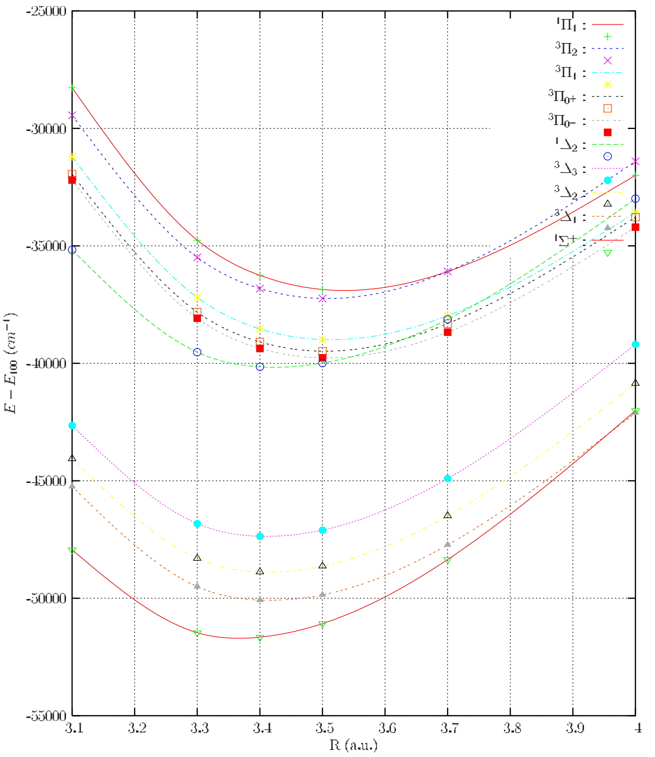

FIG. 1. (Color online) Calculated potential energy curves of the HfF$^+$.

TABLE IV. Transition energies (in cm^{-1}) from the terms of the $5d^16s^1$ configuration to the $5d^06s^2$ configuration obtained in RCC calculations of the Hf^{2+} ion.

Transition from	10-electron calculation	16-electron calculation	24-electron calculation	Contribution from $5s5p$	Contribution from $4f$
$6s_{1/2}5d_{3/2}(J=1)$	9233	10899	9182	−1717	−51
$6s_{1/2}5d_{3/2}(J=2)$	8935	11353	8817	−2536	−118
$6s_{1/2}5d_{5/2}(J=2)$	6251	8763	6036	−2727	−215
$6s_{1/2}5d_{5/2}(J=3)$	5168	6991	4973	−2018	−195

shells, the difference between the 24-electron and 10-electron calculations gives us the contribution of the correlation with accounting for the $4f$ shell. One can see from Table IV that influence of the $4f$ correlation is about one order of magnitude smaller than that of the $5s5p$ correlation. In the framework of the "atom-in-a-molecule" model, the $5d^{1}6s^{1}\to 5d^{0}6s^{2}$ excitation of the Hf^{2+} fragment gives the leading contribution to the $^{1}\Sigma^{+}\to{}^{3}\Delta_{1}$ transition of HfF^{+}. Therefore, we do not expect changes more than 100 cm^{-1} in the energy for the above transition when $4f$ correlation and relaxation are taken into account. Thus we do not expect that the order of levels will be changed. Accounting for correlation of the $4f^{14}$ shell will hardly change the calculated lifetime of the $^{3}\Delta_{1}$ state (see below) by more than 20%. The obtained data are in good agreement with the suggestions given in [8].

Considering the strongest transitions from the data of Table II we can suggest that the most convenient schemes for populating the $^{3}\Delta_{1}$ state by the laser beam are $^{1}\Sigma^{+}\to{}^{3}\Pi_{1}\to{}^{3}\Delta_{1}$ and $^{1}\Sigma^{+}\to{}^{3}\Pi_{0+}\to{}^{3}\Delta_{1}$.

In Table V we have tabulated the lifetimes τ_{el} and τ_{vibr} for the lowest vibrational levels of the $^{3}\Delta_{1}$. The correction factors $[D^{10e}(3.4)/D^{20e}(3.4)]^{2}$ calculated from the data of Tables I and II for τ_{el} and τ_{vibr} are 0.673 and 1.028, respectively. The lifetime of the zero vibrational level of the $^{3}\Delta_{1}$ is sufficient for the experiment. This level is, probably, more appropriate for experiment because the excited vibrational levels have rather fast vibrational relaxation.

TABLE V. Calculated vibrational energy levels (in cm^{-1}) of the $^{1}\Sigma^{+}$ and $^{3}\Delta_{1}$ states and radiational lifetimes (in seconds) of the $^{3}\Delta_{1}$ state.

v	$^{1}\Sigma^{+}$	$^{3}\Delta_{1}$	$^{3}\Delta_{1}$	$^{3}\Delta_{1}$
	E_{v}	E_{v}	τ_{el}	τ_{vibr}
0	416	368	0.389	
1	1234	1117	0.365	0.184
2	2038	1878	0.343	0.088
3	2821	2631	0.316	0.059
4	3586	3373	0.290	0.046

IV. CONCLUSION

Our study shows that accounting for correlation of the $4f^{14}$ shell of Hf will not seriously change the spectroscopic parameters calculated for HfF^{+} in [8]. The $^{3}\Delta_{1}$ state is obtained as relatively long lived, with the lifetime equal to about 0.4 s. This state can be easily populated by the laser beam from the ground state through the intermediate $^{3}\Pi_{0+}$ or $^{3}\Pi_{1}$ states. Accounting for the large E_{eff} value we conclude that the HfF^{+} cation is a promising candidate for the *e*EDM experiment.

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