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Dipole allowed transitions in GdF: A four-component relativistic general open-shell configuration interaction study

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A four-component relativistic study of electronic transitions in the gadolinium monofluoride molecule (GdF) is presented. The electronic spectra of GdF have been investigated with a general open-shell configuration interaction method, where active electrons are distributed among molecular spinors mainly consisting of the Gd $4f$, $5d$, and $6s$ atomic spinors. The near-degeneracy effects of these spinors on the molecular electronic structure are considered by the valence full-CI-like approach. By the magnitudes of calculated transition dipole moments, the candidates for the observable transitions were selected. The present result is complementary to our previous study based on multireference configuration interaction singles and doubles calculations, which identified the electronic excited states of GdF by comparing the calculated excitation energies and angular momenta with those given by the laser spectroscopy. The spectra of the excited states less than 3.0 eV have been refined with the help of the calculated transition probabilities. The transitions between the excited states are newly analyzed and a rearrangement is proposed. © 2008 American Institute of Physics. [DOI: 10.1063/1.3039794]

I. INTRODUCTION

The electronic spectra of lanthanide fluorides have been investigated experimentally by several groups.¹⁻⁷ In particular, Kaledin *et al.*⁷ performed an intensive investigation of the GdF molecule. Most of the excited states of GdF up to about 3.0 eV above the ground state have been characterized by them. They also performed ligand field theory (LFT) calculations which gave results consistent with experiment, but some uncertainties still remain.

Several computational studies of the ground state of GdF (Refs. 8–14) have been published. However, studies of the excited states are scarce. We therefore performed *ab initio* all-electron four-component configuration interaction (CI) calculations on GdF in a previous paper¹⁵ to clarify its electronic spectrum. This CI was multireference CI singles and doubles (MRCISD) based on the reduced frozen core approximation.^{16,17} The number of the reference functions was in the range from one to five. The active spinors in the CI calculations were as follows:

Gd: $[\text{Cd}](5p)^6(6s)^2(5d)^1(4f)^7 (25/18/15/10/1)/[2/5/4/5/1]$
for $(s_+/p_+/d_+/f_+/g_+)$,

F: $[\text{He}](2s)^2(2p)^5 (12/8/2)/[3/5/2]$
for $(s_+/p_+/d_+)$.

Here, the numbers in parentheses and in square brackets show primitive and contracted Gaussian-type functions, respectively.

The result of this MRCISD calculation is summarized in Table IX of the previous paper.¹⁵ Let us repeat its essence. The ground state of GdF is written as Gd^+F^- ($\Omega=7/2$), where the electronic configuration of Gd is $(4f)^7(6s)^2$. A $5d$ electron of Gd is moved to F. The excited state designated as [15.8] observed 1.956 eV (15776.9 cm^{-1}) above the ground state is calculated to be $\Omega=7/2$, $(4f)^7(5d_+)^1(6s)^1$ of excitation energy 1.829 eV, being in good agreement with the assignment by Kaledin *et al.*⁷ Similarly, the excited state designated as [18.3] observed at 2.264 eV ($18\,261.9 \text{ cm}^{-1}$) is calculated to be $\Omega=9/2$, $(4f)^7(5d_-+5d_+)^1(6s)^1$ of excitation energy 1.974 eV. Its angular momentum ($\Omega=9/2$) did not agree with $\Omega=7/2$ assigned by Kaledin *et al.*

In the previous MRCISD study we identified the excited states on the basis of their excitation energies and their Ω values. The result is mostly consistent with the assignment by Kaledin *et al.*⁷ However, the spectra are very complicated and therefore the assignment based merely on the excitation energies and angular momenta has some uncertainties. In addition, the $4f$ molecular spinors are nearly degenerate and the $4f$ electrons can easily have various configurations of $^8\Sigma^-$. However, MRCISD with only a few reference functions cannot treat such a multiconfigurational effect, which suggests that MRCISD with more reference functions or multi-electron excitation CI (such as valence full CI) is needed to clarify the electronic structure of the excited states. In addition, the observed transitions between the excited states are left unresolved.

In order to solve the problems described above, we have in the present study performed *ab initio* all-electron four-component general open-shell CI (GOSCI) calculations,

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where the full configurations are generated within the $(4f)$ and $(5d, 6s)$ spaces. This type of CI yields many configurations, and accordingly increases the number of possible transitions between states, which in turn complicates the analysis. We have developed a code to calculate transition density matrices and transition dipole moments in a development version of the DIRAC program system.¹⁸ This program helps us to eliminate unimportant transitions based on the transition probabilities and enables us to concentrate our attention on the analysis of the promising candidates for the observed transitions. Since the electron correlation effects are not fully considered at the GOSCI level, this elimination is critical to secure the reliability of the assignment.

II. METHOD OF CALCULATION

We used the Koga, Tatewaki, and Matsuoka (KTM) basis set¹³ as in the previous MRCISD study,¹⁵ but this time it was employed as primitive Gaussian-type functions (pGTFs) without contractions. The exponents for the L_- ($j=l-1/2$) spinors are used for the L_+ ($j=l+1/2$) spinors as well. For Gd two p functions of exponents 0.050 and 0.019 (Ref. 19) and two g functions of exponents 5.35 and 2.67 are further added, and for F two d functions of exponents 3.559 and 0.682,¹⁹ yielding a total of 362 and 817 pGTFs for the large and the small components, respectively. The total basis set is as follows:

Gd: $(25s\ 21p\ 16d\ 10f\ 2g)$,

F: $(12s\ 8p\ 2d)$.

We used the uniform nuclear model throughout the paper. All the Hartree–Fock (HF) and GOSCI calculations, based on the Dirac–Coulomb (DC) Hamiltonian, were done with the DIRAC program system. The GOSCI module is an extended version of the COSCI (complete open-shell CI) program²⁰ originally implemented to the MOLFDIR program suite²¹ and, as pointed out in the Introduction, we have extended it by a code for the calculation of transition density matrices and transition dipole moments. The transition probability A_{ij} (s^{-1}) is evaluated according to the following formula,²² where μ_{ij} is the norm of transition dipole moment (Debye) and $\bar{\nu}_{ij}$ is the energy difference (cm^{-1}) between states i and j .

$$A_{ij} = \frac{8\pi^2}{3\hbar\epsilon_0} |\mu_{ij}|^2 \bar{\nu}_{ij}^3 = 3.137 \times 10^{-7} |\mu_{ij}|^2 \bar{\nu}_{ij}^3. \quad (1)$$

The calculations were carried out in C_{2v} symmetry. However, the spinors are classified according to the projection of total angular momentum (ω) on the molecular axis and the CI Hamiltonian is explicitly constructed and diagonalized for each block of Ω .

As the active spinors of GOSCI, the 26 molecular spinors, corresponding to 13 Kramers pairs, consisting mainly of the Gd $4f$, $5d$, $6s$, and $6p$ atomic spinors were selected. The CI space is generated by a direct product of two spaces, i.e., $(4f)^7 \otimes (5d, 6s)^2$; one is generated by distributing seven electrons in 14 spinors mainly composed of Gd $4f$ atomic spinors and the other by distributing two elec-

trons in 12 spinors mainly composed of Gd $5d$, and $6s$, and $6p$ atomic spinors. This restriction was introduced in order to make the CI calculation feasible by reducing the total number of Slater determinants and is critical because the current GOSCI module stores and keeps the CI matrix in the main memory and diagonalizes it with the in-core algorithm.

The ground state of GdF is $(4f)^7(6s)^2$ and most of its low-lying excited states are $(4f)^7(5d)^1(6s)^1$ and $(4f)^7(5d)^2$ as shown by the experiment of Kaledin *et al.*⁷ Separating the $(4f)$ and $(5d, 6s)$ manifolds is therefore permissible as a first approximation. However, the ${}^8\Phi_{13/2} (4f)^8(6s)^1$ state is expected by their LFT calculations at 2.388 eV ($19\ 259\ cm^{-1}$) above the ground state,⁷ which is not so high. Although the ground state²³ of the Gd cation (Gd^+) is ${}^{10}D_{5/2}$ of the $(4f)^7(5d)^1(6s)^1$ configuration, its first excited state (${}^8F_{13/2}$) of the $(4f)^8(6s)^1$ configuration is observed at 0.991 eV ($7992.3\ cm^{-1}$) above the ground state.²³ Despite these facts we have chosen to neglect $(4f)^8$ configurations in the present GOSCI calculations. By this separation the total number of Slater determinants becomes 19 798 for the case of $\Omega=1/2$, for example. Since we are mainly interested in the dipole transitions between the low-lying excited states where $(4f)^8$ does not play an important role, we conclude that the neglect of $(4f)^8$ is reasonable.

In the previous MRCISD study,¹⁵ an HF/DC spinor set optimized for the neutral GdF molecule was used. However, in the present study, a spinor set obtained from an HF/DC average-configuration $(4f)^7(6s)^1$ of GdF^+ is used. The reason why we used a cation spinor set is that the SCF procedure for HF/DC did not converge for the neutral system $(4f)^7(6s)^2$. On the other hand, such cation spinor sets gave spectroscopic constants and excitation energies for LaF (Ref. 24) and CeF (Ref. 25) consistent with experiment.

Vertical excitation energies (T_v) and transition dipole moments are evaluated at the equilibrium internuclear distance $R_e=3.7599$ a.u. obtained by GOSCI. To obtain potential energy curves (PECs), we have performed calculations at the six internuclear distances from 3.25 until 4.50 a.u. with a grid spacing of 0.25 a.u. Vibrational constants such as R_e , ω_e , $\omega_e x_e$, etc., are obtained from cubic natural spline curves fitted to the GOSCI total energy values. T_e (calculated from the potential minima) and T_0 (calculated from the potential minima + $1/2\hbar\omega$) are also evaluated. The term value of upper (lower) state is denoted by T' (T'') and the transition energy ($T' - T''$) by ΔT . Similarly $\Delta\Omega$ is defined as $(\Omega' - \Omega'')$. The state numbers in the full space (SN in tables) are ordered according to the T_v values. The state number for a given Ω is denoted by N .

III. RESULTS AND DISCUSSION

A. Transitions between the ground state and excited states

1. The ground state

At the GOSCI level, the lowest energy state is found to be $\Omega=7/2$. The CI total energy is $-11\ 374.421\ 964$ a.u.. However, as shown in Table I, the energy difference between $\Omega=7/2$ and $\Omega=5/2$, $3/2$, $1/2$ is less than 0.001 eV ($10\ cm^{-1}$); the small energy differences in $\Omega=7/2$, $5/2$, $3/2$,

TABLE I. The ground state and its near-degenerate states.

SN	Ω	N	T_v (eV)	T_v (cm ⁻¹)
1	7/2	1	0.0	0.0
2	5/2	1	0.000	4.0
3	3/2	1	0.001	6.7
4	1/2	1	0.001	8.1

1/2 indicate that they all arise from the atomic $(4f)^7 8S$ configuration. Kaledin *et al.*⁷ determined the ground state as $8\Sigma^-$. The previous HF/DC study by Tatewaki and Matsuoka¹⁰ as well as our previous MRCISD study¹⁵ also support $\Omega = 7/2$. Other researchers^{8,9,11-14} have also assumed $\Omega = 7/2$. We regard the ground state as $\Omega = 7/2$ also in this study. It should be noted that the designation $(4f)^7(6s)^2$ is symbolic and the actual $6s$ molecular spinor has some contributions from Gd $5d$ and $6p$ atomic spinors.

In the case of $\Omega = 7/2$, the GOSCI solution of the lowest total energy has a multiconfigurational nature; 79 determinants have CI coefficients whose squares are larger than 0.001 and the largest square among them is only 0.1473.

Since we are more interested in the excited states than the ground state, we will not analyze in detail the ground state. However, comparing the calculated properties of the ground state with experiment or with the computational results of other researchers would be meaningful to assess the accuracy of our calculation. The calculated dissociation energy (D_e) is 5.31 eV is in reasonable agreement with the experimental value (6.95 eV),²⁶ the previous MRCISD value (5.27 eV),¹⁵ the CCSD(T) value (6.36 eV),¹⁴ and the CISD+Q value (6.24 eV).¹² The calculated equilibrium bond length (R_e) 3.760 a.u. (1.990 Å) agrees with the experimental value (1.959 Å),⁷ the previous MRCISD value (1.972 Å),¹⁵ the CCSD(T) value (1.97 Å),¹⁴ and the CISD+Q value (1.963 Å).¹² The CCSD(T) and CISD+Q values are given by scalar relativistic calculations neglecting spin-orbit coupling. However, the value of ω_e (565.2 cm⁻¹) is rather small comparing with the experimental value (611 cm⁻¹) cited in Ref. 9. It is also small in comparison

with our previous HF/DC value (675 cm⁻¹) (Ref. 13) as well as our MRCISD value (674 cm⁻¹).¹⁵ Although it is a peculiar feature for the valence full-CI-like methods that the calculated ω_e values are small, this discrepancy indicates that the accuracy of the present calculation is at the semiquantitative level due to the insufficient consideration of the electronic correlation effects. Hence we must be careful in analyzing the excited states in subsequent sections and must proceed with the help of the previous MRCISD results.¹⁵

2. Excited states around 0.55 eV

Kaledin *et al.*⁷ found ten forbidden bands around 0.548 eV (4416 cm⁻¹). We searched states in the range from 0.01 to 0.7 eV and also found ten states. They are listed in Table II with their gross atomic orbital populations (GAOPs). Hereafter atomic spinors are surrounded with square brackets to distinguish them from molecular spinors noted by parentheses. As shown in Table II, the states are concentrated in the energy region from 0.44 to 0.57 eV. They are generated mainly by combining $\Omega = 7/2$ of $(4f)^7$ and $(\Omega = 3, 2, 1)$ of $(5d)^1(6s)^1$. All of them have small transition probabilities with the ground state, which agrees with the fact that the direct transitions from the ground state are not observed experimentally. By comparing the ground state population $[4f]^7[6s]^{1.5}[5d]^{0.3}[6p]^{0.2}$ with the excited state populations $[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$, one can recognize that these transitions occur from the excitations from $6s$ to $5d$ atomic spinors. This is a reason why the transition dipole moments are small. We may also explain this by the lower $(5d)^1(6s)^1$ configurations being tripletlike with respect to the ground state. That the calculated transition energies increase as the Ω value varies from 5/2, 3/2, 1/2, 1/2, 3/2, 5/2, 7/2, 9/2, 11/2, to 13/2 agrees well with the LFT calculations of Kaledin *et al.*

One may doubt the accuracy of the calculated transition dipole moments (probabilities) since the diffuse pGTFs are not included in the basis set. We tried to use the set including the diffuse pGTFs but failed to obtain the converged SCF solutions. We therefore cannot clarify the effects of the diffuse pGTFs for GdF. We found for the other molecule YF

TABLE II. Excited states below 0.55 eV.

SN	Ω	N	Population	T_0 (eV)	T_0^a (eV)	T_0^a (cm ⁻¹)	D_e^b (eV)	R_e (a.u.)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Tr-mom ^c (D)	Tr-prob ^c (s ⁻¹)
1	7/2	1	$[4f]^7[6s]^{1.5}[5d]^{0.3}[6p]^{0.2}$	0.0	0.0	0	5.306	3.760	565.2	-5.3	—	—
5	5/2	2	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.436	0.245	1978	4.866	3.863	504.3	-1.1	0.505	0.122
6	3/2	2	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.448	0.263	2121	4.855	3.862	504.4	-1.2	—	—
7	1/2	2	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.460	0.281	2269	4.842	3.862	504.4	-1.2	—	—
8	1/2	3	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.472	0.301	2426	4.830	3.861	504.5	-1.2	—	—
9	3/2	3	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.485	0.321	2590	4.817	3.860	504.6	-1.3	—	—
10	5/2	3	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.499	0.343	2764	4.803	3.859	504.7	-1.3	0.000	0.000
11	7/2	2	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.513	0.366	2950	4.789	3.859	504.8	-1.3	0.001	0.000
12	9/2	1	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.528	0.391	3150	4.834	3.858	505.0	-1.4	0.003	0.000
13	11/2	1	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.544	0.417	3367	4.818	3.857	505.3	-1.4	—	—
14	13/2	1	$[4f]^7[6s]^{0.8}[5d]^{1.1}[6p]^{0.1}$	0.561	0.447	3608	4.850	3.856	505.6	-1.5	—	—

^a T_0 values from LFT calculations by Kaledin *et al.* (Ref. 7).^bDissociation energy is calculated from $\{\text{TE}(\text{Gd}; 4f^7 5d^1 6s^2 D(\Omega_1)) - \text{TE}(\text{F}; 2p^5 P(\Omega_2))\}_{\Omega=\Omega_1+\Omega_2} - \text{TE}(\text{GdF}(\Omega))$ at respective R_e .^cThe dashes denote forbidden transitions.

TABLE III. Vertical excitation energies (T_v) in the range from 0.7 to 3.0 eV and the transition dipole moments (entries of which transition moments are larger than 2.5 D are listed in bold type).

SN	Ω	N	T_v (eV)	Tr-mom (D)	SN	Ω	N	T_v (eV)	Tr-mom (D)	SN	Ω	N	T_v (eV)	Tr-mom (D)
15	7/2	3	0.782	0.147	52	9/2	6	1.763	0.034	94	7/2	14	2.309	0.739
16	5/2	4	0.796	0.113	53	7/2	9	1.766	0.005	95	9/2	10	2.322	0.158
21	5/2	5	0.879	0.009	54	5/2	11	1.769	0.020	96	5/2	19	2.406	0.770
22	7/2	4	0.899	0.043	62	5/2	12	1.848	0.505	99	7/2	15	2.407	0.299
23	9/2	2	0.922	0.184	63	9/2	7	1.850	0.247	102	5/2	20	2.423	0.342
29	5/2	6	1.089	0.000	64	7/2	10	1.855	0.232	103	7/2	16	2.424	0.238
30	7/2	5	1.110	0.002	65	7/2	11	1.858	0.308	104	9/2	11	2.424	0.606
31	9/2	3	1.131	0.003	66	5/2	13	1.861	0.081	106	5/2	21	2.467	0.530
33	9/2	4	1.259	0.374	74	5/2	14	2.003	0.034	108	7/2	17	2.499	4.537
34	7/2	6	1.276	0.072	75	5/2	15	2.019	4.534	109	5/2	22	2.502	0.039
35	5/2	7	1.287	0.115	77	7/2	12	2.030	0.000	115	5/2	23	2.542	0.004
38	5/2	8	1.317	0.562	81	9/2	8	2.059	0.556	116	7/2	18	2.550	0.084
43	5/2	9	1.407	0.079	82	5/2	16	2.061	0.374	117	9/2	12	2.556	0.045
44	7/2	7	1.424	0.102	83	7/2	13	2.068	0.013	123	5/2	24	2.787	0.000
45	9/2	5	1.446	0.142	84	9/2	9	2.075	4.850	124	7/2	19	2.805	0.000
46	7/2	8	1.625	0.164	88	5/2	17	2.180	1.126	125	9/2	13	2.826	0.007
47	5/2	10	1.659	0.092	93	5/2	18	2.301	0.194					

that the sets with the diffuse pGTFs bring 50% changes in the ground state dipole moment than the set without them. The effects of the diffuse functions are not so large as we worried. Moreover, since we are concerned whether the state is observed or not, the relative values of the transition probabilities are important. We may find our discussion is quite safe if we compare the transition probabilities in Tables II with those in Table IV.

In the previous MRCISD study,¹⁵ we proposed three candidates for the states around 0.55 eV. The most promising one was $\Omega=13/2$, $(4f)^7(5d)^1(6s)^1$ of $T_0=0.582$ eV, the others being $\Omega=5/2$ of $T_0=0.494$ eV and $\Omega=9/2$ of $T_0=0.652$ eV. All these three states are included in Table II and are retained as candidates even after the present refinement. The present GOSCI calculation gives $T_0=0.561$ eV for $\Omega=13/2$. This value of T_0 is close to the previous MRCISD result of 0.582 eV.

3. The [15.8] state

Kaledin *et al.*⁷ observed a strong band of 1.956 eV (15 776.9 cm^{-1}) and designated it as [15.8]. They found another strong band of 2.264 eV (18 261.9 cm^{-1}) and designated it as [18.3]. Since these bands are transitions to the $\Omega=7/2$ ground state, we searched CI solutions of $\Omega=5/2$,

7/2, or 9/2. There are 50 states whose vertical transition energies (T_v) are in the range from 0.7 to 3.0 eV and they are listed in Table III with the transition dipole moments. Among them only three states have transition dipole moments greater than 2.5 D. These three states are listed in bold type in Table III and their details are listed in Table IV. Their PECs are shown in Fig. 1. The calculated values of T_0 are 2.020 eV ($\Omega=5/2$), 2.073 eV ($\Omega=9/2$), and 2.434 eV ($\Omega=7/2$), respectively. From the energetical point of view, the lower two states should be considered as the [15.8] state and the uppermost state as the [18.3] state. The large values of $\omega_e x_e$ in Table IV are due to the shallow double minimum on their PECs in Fig. 1.

The populations of the $\Omega=5/2$ and $\Omega=9/2$ states are $[4f]^7[6s]^{0.5}[5d]^{0.9}[6p]^{0.6}$ and $[4f]^7[6s]^{0.4}[5d]^{0.9}[6p]^{0.6}$, respectively. The contributions from the atomic $6p$ spinors are significant. Comparing these with the ground state population $[4f]^7[6s]^{1.5}[5d]^{0.3}[6p]^{0.2}$, we recognize that the [15.8] state is described mainly by a transition from the atomic $6s$ to atomic $6p$ and $5d$ spinors.

In the previous MRCISD study, we identified the $\Omega=7/2$ as [15.8]. However, we should have regarded the $\Omega=5/2$ state of $T_0=1.954$ eV and the $\Omega=9/2$ state of $T_0=1.972$ eV given by MRCISD as the [15.8] state straightforwardly. The electronic configuration $(4f)^7(5d_-+5d_+)^1(6s_+)^1$

TABLE IV. Candidates for the [15.8] and [18.3] states.

SN	Ω	N	Population	T_0 (eV)	T_0^a (eV)	T_0^b (eV)	T_0^b (cm^{-1})	D_e^c (eV)	R_e (a.u.)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	Tr-mom (D)	Tr-prob (s^{-1})
1	7/2	1	$[4f]^7[6s]^{1.5}[5d]^{0.3}[6p]^{0.2}$	0.0	0.0	0.0	0	5.306	3.760	565.2	-5.3	—	—
75	5/2	15	$[4f]^7[6s]^{0.5}[5d]^{0.9}[6p]^{0.6}$	2.020	1.954	1.956	15776.9	3.287	3.775	691.6	237.5	4.534	2.79E+07
84	9/2	9	$[4f]^7[6s]^{0.4}[5d]^{0.9}[6p]^{0.6}$	2.073	1.972	1.956	15776.9	3.291	3.782	656.1	242.4	4.850	3.46E+07
108	7/2	17	$[4f]^7[6s]^{0.6}[5d]^{0.9}[6p]^{0.5}$	2.434	2.548	2.264	18261.9	2.865	4.158	516.3	115.7	4.537	5.29E+07

^a T_0 values obtained from our previous MRCISD calculations (Ref. 15).^bExpt. (Ref. 7).^cDissociation energy is calculated from $\{\text{TE}(\text{Gd}; 4f^7 5d^1 6s^2 \text{D}(\Omega_1)) - \text{TE}(\text{F}; 2p^5 \text{P}(\Omega_2))\}_{\Omega=\Omega_1+\Omega_2} - \text{TE}(\text{GdF}(\Omega))$ at respective R_e .

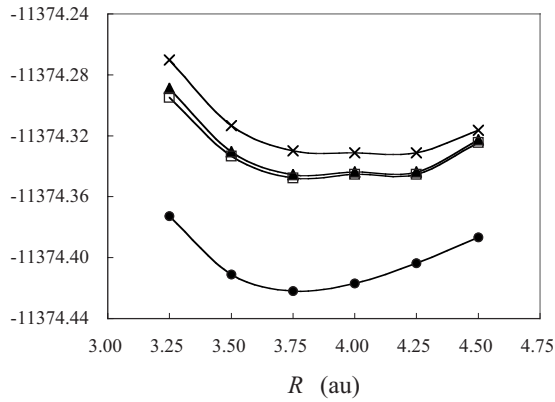


FIG. 1. PECs of the ground state and two candidate states for the [15.8] state and one for the [18.3] state. Cross: ($\Omega=7/2, N=17$). A candidate state for [18.3]. Solid triangle: ($\Omega=9/2, N=9$). A candidate state for [15.8]. Open rectangle: ($\Omega=5/2, N=15$). A candidate state for [15.8]. Solid circle: ($\Omega=7/2, N=1$). The ground state.

which both states was considered to have is consistent with the present characterization. Thus, it is quite reasonable to regard these two states having close energies as the [15.8] states.

The double-minimum PECs shown in Fig. 1 can be ascribed to the mixing of two configuration groups of $(4f)^7(5d)^1(6s)^1$ and $(4f)^7(5d)^2$. The details are given in the Appendix.

4. The [18.3] state

The $\Omega=7/2$ state of $T_0=2.434$ eV in Table IV has a population of $[4f]^{7.0}[6s]^{0.6}[5d]^{0.9}[6p]^{0.5}$. This is consistent with the assignment of Kaledin *et al.*⁷ The present value of T_0 is somewhat larger than the experimental value of 2.264 eV, but if we consider the fact that the T_0 value (2.548 eV) of the corresponding $\Omega=7/2$ in the previous MRCISD study is the same as the present value, this discrepancy of 0.2 eV is within a permissible range. We find no other strong transitions in this energy region, and the $\Omega=7/2$ state of Table IV should therefore be regarded as the [18.3] state.

As shown in Fig. 1, the double-minimum potential is diminished. This can be ascribed to the larger weight of the

configuration group of $(4f)^7(5d)^1(6s)^1$ in the [18.3] state. (See Appendix) The diminishing of the double-minimum in the PEC gives $\omega_e x_e$ smaller than those of the [15.8] state as shown in Table IV.

B. Transitions between excited states

Generally speaking, there are three cases for the transitions between the excited states according to the selection rule, i.e., $\Delta\Omega = \pm 1$ and 0. Kaledin *et al.*⁷ observed $\Delta\Omega = +1$ transitions in the near-infrared region and $\Delta\Omega=0$ transitions in the visible region, but they reported nothing about the $\Delta\Omega=-1$ case. Let us start the discussion from the $\Delta\Omega = +1$ case.

1. $\Delta\Omega = +1$ (near-infrared region)

Kaledin *et al.* identified six bands in the near-infrared region ($\sim 13\,666\text{ cm}^{-1}$) as the transitions of $\Delta\Omega = +1$ as listed in the 11th and 12th columns of Table V. In this energy region we searched $\Delta\Omega = +1$ transitions whose calculated transition dipole moments are greater than 50% of the maximum one (2.5 D). We find ten transitions. We classified them into two groups so that ΔT_0 decreases by about 0.01 eV with decreasing Ω'' . We call these groups *sequences* from now on. These two sequences are listed in Table V. The first sequence begins from $\Delta T_0 = 1.560$ eV and the second sequence from 1.894 eV. The energy gap between them is as large as 0.311 eV. In both sequences, the upper states have a population of $[4f]^{7.0}[5d]^{1.4}[6p]^{0.5}$. It should be noted that all the lower states here are the low-lying excited states which appear as the entries of Table II with populations of $[4f]^{7.0}[5d]^{1.1}[6s]^{0.8}[6p]^{0.1}$.

The first member of the first sequence is a transition from the first $\Omega=15/2$ state to the first $\Omega=13/2$ state. The first $\Omega=15/2$ state is located 2.121 eV above the ground state and the first $\Omega=13/2$ state 0.561 eV (T_0) above the ground state. Since the corresponding experimental ΔT_0 value is 1.732 eV, the calculated ΔT_0 value (1.560 eV) is a little smaller than the experimental value. The calculated transition energy decreases by about 0.01 eV as Ω'' decreases

TABLE V. Transitions between the excited states ($\Delta\Omega = +1$).

SN'	Ω'	N'	SN''	Ω''	N''	Population	T_0' (eV)	T_0'' (eV)	ΔT_0 (eV)	ΔT_0^a (eV)	ΔT_0^a (cm^{-1})	R_e (a.u.)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	Tr-mom (D)	Tr-prob (s^{-1}) ($\times 10^{+07}$)
Seq-1																
87	15/2	1	14	13/2	1	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.5}$	2.121	0.561	1.560	1.732	13973	3.894	483.0	0.3	4.882	0.93
86	13/2	2	13	11/2	1	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.5}$	2.083	0.544	1.539	1.719	13861	3.893	483.4	0.3	4.861	1.47
85	11/2	5	12	9/2	1	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	2.048	0.528	1.520	1.706	13759	3.893	483.9	0.3	4.850	1.41
81	9/2	8	11	7/2	2	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	2.019	0.513	1.506	1.694	13667	3.901	456.7	-0.6	4.811	1.34
77	7/2	12	10	5/2	3	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	1.989	0.499	1.490	1.683	13578	3.896	473.8	-1.7	4.826	1.30
74	5/2	14	9	3/2	3	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	1.962	0.485	1.477	1.673	13497	3.901	486.0	1.0	4.822	1.27
73	3/2	18	8	1/2	3	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	1.932	0.472	1.460	—	—	3.897	558.7	4.1	4.808	1.23
Seq-2																
99	7/2	15	5	5/2	2	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	2.330	0.436	1.894	—	—	3.937	502.4	2.3	4.708	2.68
96	5/2	19	6	3/2	2	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	2.330	0.448	1.882	—	—	3.939	495.3	1.9	4.096	1.99
97	3/2	23	7	1/2	2	$[4f]^{7.0}[5d]^{1.4}[6p]^{0.6}$	2.331	0.460	1.871	—	—	3.943	475.3	1.5	3.754	1.64

^aExpt. (Ref. 7).

TABLE VI. Transitions between the excited states ($\Delta\Omega=-1$).

SN'	Ω'	N'	SN''	Ω''	N''	Population	T_0' (eV)	T_0'' (eV)	ΔT_0 (eV)	R_e (a.u.)	ω_e (cm ⁻¹)	$\Omega_e x_e$ (cm ⁻¹)	Tr-mom (D)	Tr-prob (s ⁻¹) ($\times 10^{+07}$)
Seq-1														
105	11/2	6	14	13/2	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.6}$	2.347	0.561	1.786	3.945	474.8	1.8	5.086	2.65
104	9/2	11	13	11/2	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.6}$	2.348	0.544	1.804	3.941	476.4	1.2	4.774	2.39
103	7/2	16	12	9/2	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.6}$	2.350	0.528	1.822	3.938	478.2	1.2	4.282	1.97
102	5/2	20	11	7/2	2	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.6}$	2.348	0.513	1.835	3.937	486.8	1.6	3.966	1.73
101	3/2	24	10	5/2	3	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.6}$	2.348	0.499	1.849	3.936	484.2	1.3	3.589	1.44
98	1/2	24	9	3/2	3	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.6}$	2.331	0.485	1.846	3.937	505.8	2.4	2.893	0.94
100	1/2	25	9	3/2	3	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.6}$	2.317	0.485	1.832	3.936	479.3	0.7	3.099	1.10
Seq-2														
70	3/2	17	5	5/2	2	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.5}$	1.891	0.436	1.455	3.853	557.2	-0.7	4.616	1.07
71	1/2	18	6	3/2	2	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.6}$	1.899	0.448	1.451	3.873	556.3	-0.9	4.708	1.13

by 1. This energetics of this sequence agrees well with the observed features. (See the column termed “ $^{10}\Phi_{\Omega+1}-a^{10}\Delta_{\Omega}$ Transition $\nu^{\text{Exp.}}$ ” in Table IX of Ref. 7.)

The first member of the second sequence is a transition from the fifteenth $\Omega=7/2$ state to the second $\Omega=5/2$ state. The 15th $\Omega=7/2$ state and the second $\Omega=5/2$ state are located 2.330 and 0.436 eV above the ground state, respectively. Since the calculated transition energies are rather large to be considered as the near-infrared energy region, we exclude this second sequence from the candidates for the near-infrared bands. Kaledin *et al.* did not report these transitions in the visible region.

2. $\Delta\Omega=-1$

In the same manner as in the preceding section, we search $\Delta\Omega=-1$ transitions whose transition dipole moment is larger than 2.5 D. We find nine transitions. They are listed in Table VI. We classify them into two sequences. The first sequence begins at $\Delta T_0=1.786$ eV and the second sequence at $\Delta T_0=1.455$ eV. In the first sequence ΔT_0 increases as Ω'' decreases. Reversely, in the second sequence ΔT_0 decreases. The energy gap between them is as large as 0.331 eV. All the lower states here are the low-lying excited states which ap-

pear in Table II. The large transition probabilities suggest the existence of strong bands, but Kaledin *et al.*⁷ reported no such observations.

3. $\Delta\Omega=0$ (visible region)

Kaledin *et al.*⁷ observed five transitions between the excited states in the visible region (14 389–17 075 cm⁻¹). They assigned them as $^{10}\Delta((4f)^7(5d)^2)-a^{10}\Delta((4f)^7(5d)^1(6s)^1)$ of $\Delta\Omega=0$. However, as they admit that their assignment is tentative, their assignment has some uncertainties. As listed in the column termed “ $^{10}\Delta_{\Omega}-a^{10}\Delta_{\Omega}$ transition $\nu^{\text{Exp.}}$ ” in Table IX of Ref. 7, the observed transition energies are 2.117 eV (17 075 cm⁻¹, $\Omega''=5/2$), 2.106 eV (16 985 cm⁻¹, $\Omega''=3/2$), and 2.100 eV (16 937 cm⁻¹, $\Omega''=1/2$), 1.805 eV (14 559 cm⁻¹, $\Omega''=-3/2$), and 1.784 eV (14 389 cm⁻¹, $\Omega''=-5/2$). The former three and the latter two form two sequences.

We have searched transitions of large transition dipole moments and find nine transitions which are listed in Table VII. In all the cases, the upper states have a population of $[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$. We classify the transitions into two sequences. The first sequence starts at $\Delta T_0=1.905$ eV ($\Omega''=13/2$) and the second sequence starts at $\Delta T_0=1.944$ eV ($\Omega''=5/2$). In the first sequence ΔT_0 increases as Ω'' de-

TABLE VII. Transitions between the excited states ($\Delta\Omega=0$).

SN'	Ω'	N'	SN''	N''	Population	T_0' (eV)	T_0'' (eV)	ΔT_0 (eV)	ΔT_0^a (eV)	ΔT_0^a (cm ⁻¹)	R_e (a.u.)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	Tr-om (D)	Tr-prob (s ⁻¹) ($\times 10^{+07}$)
Seq-1															
118	13/2	3	14	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$	2.466	0.561	1.905	— (1.977)	— (15 942)	3.958	475.7	2.0	4.258	2.29
119	11/2	7	13	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$	2.468	0.544	1.924	— (2.017)	— (16 271)	3.956	476.9	1.9	4.113	2.19
117	9/2	12	12	1	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$	2.466	0.528	1.938	— (2.047)	— (16 513)	3.954	478.2	1.9	4.016	2.13
116	7/2	18	11	2	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$	2.467	0.513	1.954	— (2.070)	— (16 699)	3.935	544.6	3.0	3.944	2.08
115	5/2	23	10	3	$[4f]^{7.0}[6s]^{0.0}[5d]^{1.4}[6p]^{0.5}$	2.467	0.499	1.968	2.117 (2.089)	17 075 (16 846)	3.929	533.7	2.3	3.887	2.04
114	3/2	27	9	3	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.5}$	2.465	0.485	1.980	2.106 (2.104)	16 985 (16 970)	3.918	526.8	1.6	3.835	1.99
110	1/2	26	7	2	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.5}$	2.416	0.460	1.956	2.100 (2.036)	16 937 (16 424)	3.965	470.4	2.5	3.399	1.56
Seq-2															
106	5/2	21	5	2	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.5}$	2.380	0.436	1.944	2.117	17 075	3.961	467.4	-1.1	3.928	2.04
107	3/2	25	6	2	$[4f]^{7.0}[6s]^{0.1}[5d]^{1.4}[6p]^{0.5}$	2.400	0.448	1.952	2.106	16 985	3.965	469.0	0.9	3.837	1.97

^aExpt. (Ref. 7). The numbers in parentheses denote the T_0 values obtained from LFT calculations by Kaledin *et al.*

creases with an exception at $\Omega''=1/2$. The remaining terms are gathered into the second sequence. These two sequences lie overlapped in energy; there is no energy gap between them. This point is apparently different from the cases of $\Delta\Omega=\pm 1$. Thus, the reason for the classification is not strong. The third $\Omega'=13/2$ state is located 2.446 eV above the ground state. And the 21st $\Omega'=5/2$ state is located 2.380 eV above the ground state.

As shown in Table VII, the calculated ΔT_0 values of the higher members of the first sequence are close to the observed values. While our calculated ΔT_0 values increase in the order $\Omega''=1/2, 5/2$, and $3/2$, the observed ones increase in the order $\Omega''=1/2, 3/2$, and $5/2$. Kaledin *et al.* calculated ΔT_0 with the LFT method and their values are listed in parentheses in Table VII. LFT predicts the same order as the present work not only for the range of $\Omega''(1/2, 3/2, 5/2)$ but also for all the Ω'' states composing the first sequence. Kaledin *et al.* gave two other experimental ΔT_0 values (1.805, 1.784 eV) for $\Omega''=-5/2$ and $-3/2$ (the second sequences), but we cannot find calculated values corresponding to them. Thus, these two experimental values are not listed in Table VII.

The calculated second sequence consists of only two members, but they give ΔT_0 close to those of the first experimental sequences. In fact the ΔT_0 value (1.944 eV) for $\Omega''=5/2$ is close to the experimental ΔT_0 value (2.117 eV) as shown in Table VII.

The energy gap between the two experimental sequences is as large as 0.295 eV ($=2.100-1.805$ eV). This characteristic is not found in the calculated transition energies. We will discuss this point in more detail in Sec. III B 4.

In the previous MRCISD study, the $\Omega''=9/2$ state was considered as the most promising candidate. The calculated transition energy (ΔT_0) was 2.141 eV. And the upper and lower states were located 2.793 and 0.652 eV above the ground state, respectively. This ΔT_0 value is close to the present ΔT_0 value (1.938 eV) for $\Omega''=9/2$ in the first sequences. The previous result seems not to be in contradiction to the present result.

4. Discussion

As described in Sec. III B 3, the observed ΔT_0 values for $\Delta\Omega=0$ are close to our calculated values, but their order according to Ω values does not match ours. Their two observed values (1.805, 1.784 eV) do not fit to our values. The present calculations and the LFT calculations by Kaledin *et al.*⁷ both demonstrate that there are more bands than found in the experiment. On the other hand, concerning the $\Delta\Omega=-1$ transitions, strong bands are expected from the present calculations, while Kaledin *et al.* reported nothing about the $\Delta\Omega=-1$ case. Although there is an energy gap as large as 0.301 eV in the observed bands for $\Delta\Omega=0$, such a gap is not found in the calculated transition energies of $\Delta\Omega=0$. Instead there is an energy gap of 0.331 eV for the calculated transition energies of $\Delta\Omega=-1$.

These discrepancies seem to suggest that the ΔT_0 values (in Table VII) which Kaledin *et al.* assigned as the $\Delta\Omega=0$ case are values for $\Delta\Omega=-1$. If this is true, the energy order will match the order of the calculated ΔT_0 values in Table

VI. Namely, the members of the first sequence of $\Delta\Omega=-1$ at $\Delta T_0=1.849, 1.846$, and 1.832 eV in Table VI will correspond to the states observed at $\Delta T_0=2.117, 2.106$, and 2.100 eV of $\Delta\Omega=0$ in Table VII. (Here we assign the observed $\Delta T_0=2.100$ eV to the $\Omega''=3/2$ state in $\Delta\Omega=-1$ rather than to $\Omega''=1/2$.) Likewise the second sequence ($\Delta T_0=1.455$ eV and 1.451 eV) in Table VI to the observed transition energies (1.784 and 1.805 eV) of $\Delta\Omega=0$. The large energy gap between the first and second sequences found in our calculations would then be consistent with experiment, and thus a part of the inconsistencies would be resolved.

However, the problem that the present calculations and the LFT calculations by Kaledin *et al.* both give more bands than the observation still remains unsettled. The remaining inconsistencies need to be investigated further. Electron correlation calculations based on the multireference perturbation theory^{27,28} would be necessary for further theoretical investigations. Re-examination of the experimental data is urgently required.

IV. CONCLUSIONS

Following up our previous MRCISD calculations, we have performed GOSCI calculations on GdF. Relativistic effects are taken into consideration through the Dirac-Coulomb Hamiltonian in HF and GOSCI where the near-degeneracy effect of the $4f$ molecular spinors is considered. To compare the electronic transitions with the experimental result of Kaledin *et al.*,⁷ we have eliminated unimportant transitions with the help of the calculated transition probabilities. Comparing the present result with our previous MRCISD study,¹⁵ we have succeeded in clarifying the characters of the low-lying excited states of GdF. In particular, the characters of the [15.8] and [18.3] states have been elucidated. The transitions between the excited states have been classified according to the $\Delta\Omega$ values and a reassignment is proposed to the spectra due to the de-excitations to the states at 0.55 eV above the ground state.

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APPENDIX: WEIGHTS OF CONFIGURATION GROUPS ESTIMATED FROM GAOPs

At first we examine the HF/DC molecular spinors of the GdF cation because this spinor set is used as basis for GOSCI. The GAOPs imply that a single electron occupation of the $6s$ -like molecular spinors gives approximately $[6s]^{0.83}[5d]^{0.05}[6p]^{0.12}$. Also a single electron occupation of the $5d$ -like molecular spinors gives $[5d]^{n5d}[6p]^{n6p}$. Here atomic spinors and molecular spinors are surrounded by square brackets and parentheses, respectively. For the two $5d$ -like molecular spinors, $n5d$ is almost 1.0 (purely Ce

atomic $5d$ -like). For the remaining three $5d$ -like molecular spinors, $n5d$ and $n6p$ are around 0.5 (some atomic $6p$ -like).

We found that the three excited states of GdF (SN=75, 84, and 108 in Table IV) are almost composed of the two configuration groups of $(4f)^7(5d)^1(6s)^1$ and $(4f)^7(5d)^2$. We can approximately determine the weights of A^2 and B^2 ($=1-A^2$) for $(4f)^7(5d)^1(6s)^1$ and $(4f)^7(5d)^2$ through the GAOPs of GOSCI.

$$\begin{aligned}
 & [4f]^7[5d]^{n5d}[6p]^{n6p}[6s]^{n6s} \\
 & = A^2[4f]^7[5d]^{n5d'}[6p]^{n6p'}[6s]^{0.83} + (1-A^2) \\
 & \quad \times [4f]^7[5d]^{n5d''}[6p]^{n6p''}. \quad (\text{A1})
 \end{aligned}$$

The values of $n5d'$, $n6p'$, $n5d''$, and $n6p''$ can be obtained by simple arithmetic, but their actual values are not needed here. The values of $n5d$, $n6p$, and $n6s$ depend on the state and are listed in Table IV. Solving Eq. (A1) gives $A^2=n6s/0.83$. Then we have $A^2=0.55$, 0.54 , and 0.62 for the first ($\Omega=5/2$), the second ($\Omega=9/2$), and the third ($\Omega=7/2$) excited states. In this way, we can ascribe the double minima in the PECs shown in Fig. 1 to the contributions from the two configuration groups of $(4f)^7(5d)^1(6s)^1$ and $(4f)^7(5d)^2$.

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