Electronic Structures and Bonding of CeF: A Frozen-Core Four-Component Relativistic Configuration Interaction Study

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We study the electronic structure of the ground and several low-lying states of the CeF molecule using Dirac−Fock−Roothaan (DFR) and four-component relativistic single and double excitation configuration interaction (SDCI) calculations in the reduced frozen-core approximation (RFCA). The ground state and two low-lying excited states are calculated to have $(4f)^1(5d)^1(6s)^1$ configurations with $\Omega = 3.5$, 4.5, and 3.5, and the resulting excitation energies, T_0, are, respectively, 0.319 and 0.518 eV. The experimental configurations for these states are the same, although the experimental T_0 values are ~0.3 eV smaller than those calculated. Experimentally, the red-degraded band was observed to be 2.181 eV above the ground state, having the configuration $(4f)^1(5d)^1(6p)^1$ with $\Omega = 4.5$. The calculation for this state gives 2.197 eV and configuration $(4f)^{1.0}(5d)^{1.7}(6p)^{0.3}$ with $\Omega = 4.5$. We found that Ω, R_e, and ν(1-0) obtained by CI agree well with experiment. Bonding between the Ce and the F is highly ionic. The 4*f*, 5*d*, and 6*s* valence electrons are localized at the Ce^+ ion, because they are attracted by the Ce^{4+} ion core, and are excluded from the bonding region because of the electronic cloud around the negatively charged fluoride anion. The bonding in the ground and excited states of the CeF molecule is significantly influenced by the 6*s* and 5*d* electron distributions between the Ce and the F.

1. Introduction

Each of the lanthanides have unique optical and magnetic properties, although their chemistries are similar. These properties depend on the sizes of the ion and the configurations of 4*f*, 5*d*, and 6*s* electrons.[1] The ground states of most lanthanide atoms have $(4f)^n(6s)^2$ configurations, except for the La, Ce, and Gd atoms, which have $(5d)^1(6s)^2$, $(4f)^1(5d)^1(6s)^2$, and $(4f)^7(5d)^1(6s)^2$.[2] The ordinary electron configuration of the monovalent free cations is $(4f)^n(6s)^1$, but those of La, Ce, and Gd are $(5d)^2$, $(4f)^1(5d)^2$, and $(4f)^7(5d)^1(6s)^1$.[2]

The bonding of lanthanide monofluoride molecules (LnF) is ionic, and the lanthanide is regarded as a cation. The ground states predicted for the LnF molecules according to the ligand field theory (LFT)[3,4] have the configurations $(4f)^{n-1}(6s)^2$ for LaF, GdF, TbF, DyF, HoF, ErF, TmF, and LuF; $(4f)^n(6s)^1$ for NdF, PmF, SmF, EuF, and YbF; and $(4f)^{n-1}(5d)^1(6s)^1$ for the CeF and PrF molecules. The experimental assignments to the ground states parallel those of LFT. The presence of the F atom leads to complicated configurations in the LnF molecules; for example, La^+ in LaF is not $(5d)^2$ but $(6s)^2$, and Ce^+ in CeF is not $(4f)^1(5d)^2$ but $(4f)^1(5d)^1(6s)^1$. Careful treatment of these states is necessary when these 4*f*, 5*d*, and 6*s* spinors have similar energies.

The lanthanide monohalide (LnX) and monooxide (LnO) molecules have many low-lying excited states close together. Spin−orbit interactions among the 4*f* electrons in the lanthanides typically exceeded 1000 cm^{-1}.[2] It is expected that the split levels of states arising from $(4f)^n$ configurations due to a simple crystalline electric field are several hundred centimeters^{-1},[5] because the 4*f* electron density is largely concentrated within the 5*s* and 5*p* shell.[6] The small spin−orbit and electrostatic interactions result in densely populated low-lying states.

Laser techniques, such as magnetic rotation, fluorescence excitation, dispersed fluorescence, and wavelength-selected fluorescence excitation spectroscopy help in interpreting complicated electronic spectra.[7−10] These electronic spectra are often assigned with the help of LFT, which depends on empirical parameters.[4,11,12]

Several computational studies of electronic structures for LnX and LnO molecules have recently been published, based on LFT combined with parameters obtained by first principles calculations, for example, density functional theory,[13] multiconfiguration self-consistent field multireference configuration interaction (MCSCF-MRCI) calculations,[14] and single and multireference CI calculations with quasirelativistic pseudopotentials.[15,16] All-electron Dirac−Fock−Roothaan (DFR) calculations including the ground and excited states have been performed for the GdF and GdF_2 molecules.[17,18] Precise CI calculations analyzing GdF laser spectra were recently performed by Tatewaki and coworkers, using the same method as in the present work.[19] These studies show the importance of relativistic and correlation effects in considering the excitation energies of LnX molecules.

The chemistry of the cerium compounds differs from other lanthanides. Tetravalent cerium compounds are known as well as the trivalent ones familiar with lanthanides, and solutions of the former are widely used as oxidants. In addition to the ordinary insoluble trifluorides, tetrafluorides are important.[1]

The band transition in the CeF molecule was first recorded by Lumley.[20] This is a red-degraded band at 5679.4 Å (17610 cm^{-1}). Rotational analysis of this band yielded R_e and other spectroscopic constants of the upper (excited) and lower (ground) states.[8] Following this work, the band was assigned

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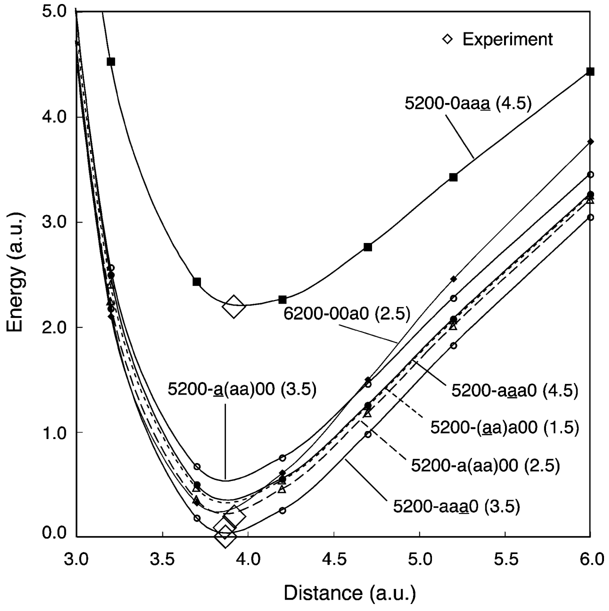

Figure 1. Potential energy curves for the ground state, several low-lying excited states, and the upper state of the red-degraded band. The experimental electronic excitation energies T_0 are also indicated with diamonds. The excited state with experimentally suggested $\Omega = 3.5$ is also shown using the calculated R_e because no experimental value is known.

as $\Omega' = 4.5 \leftarrow \Omega'' = 3.5$ based on magnetic rotation and doppler-free laser-fluorescence spectroscopy.[7,9] Two more low-lying excited states having excitation energies, T_0, 705.15 ($\Omega = 4.5$) and 1500 cm^{-1} (tentatively assigned $\Omega = 3.5$) were observed using selectively detected fluorescence excitation and dispersed fluorescence spectroscopy.[10] The experimentally observed states were only those with $\Omega = 3.5$, 4.5, and 5.5 as allowed transitions from the excited state with $\Omega = 4.5$. The observed states were all identified with the help of the LFT results.[10]

In the present work, we studied the spectroscopic constants of all of the observed states. Four-component relativistic CI calculations, which will be discussed briefly below, were performed to treat the relativistic effects directly, as well as the electron correlations. We also discuss in detail the bonding properties of the ground state. It emerges why the molecular ground state is $(4f)^1(5d)^1(6s)^1$ rather than $(4f)^1(5d)^2$.

2. Method of Calculation

All electronic structure calculations were performed using DFR and four-component relativistic single and double excitation (SD) CI calculations from a single reference configuration in the reduced frozen-core approximation (RFCA)[21,22] under the $C_{\infty v}$ double group.

2.1. RFCA. In the RFCA, the valence basis functions $\{\chi_p\}$ are orthogonalized to core spinors $\{\phi_c\}$ through corelike basis functions $\{\kappa_c\}$, to form core-orthogonalized valence basis functions $\{\omega_p\}$ as

$$\omega_p = N_p(\chi_p - \sum_c \kappa_c C_{cp}) \tag{1}$$

where N_p is a normalization constant and $\{C_{cp}\}$ are coefficients, determined such that $<\omega_p|\phi_c> = 0$. We chose the $5p_\pm$, $5d_\pm$, $6s_+$, and $4f_\pm$ spinors of Ce and the $2s_+$ and $2p_\pm$ spinors of F as valence spinors; there are 17 valence electrons in these. We used the $(25s_+18p_\pm15d_\pm10f_\pm)$[23] and $(12s_+8p_\pm)$[24] relativistic primitive sets for Ce and for F, respectively. For $(25s_+18p_\pm 15d_\pm10f_\pm)$, we used the outermost two $1s_+$-, three $2p_\pm$-, and four $3d_\pm$-like primitive Gaussian type functions (pGTFs), and five $4f_\pm$-like GTFs as the valence basis $\{\chi_p\}$, one of the latter is a contracted GTF (CGTF) composed of six 4*f*-like pGTFs. We abbreviate this to (11/111/1111/61111), where a slash separates the s_+, $p_\pm$, $d_\pm$, and $f_\pm$ symmetries. We also added two $p_\pm$ type functions[25] and two $g_\pm$ type polarization functions of which the latter have the same mean value of *r* as the $4f_\pm$ spinors.[26] The resulting Ce valence basis set is (11/1111*1*/1111/61111/1*1*), where * indicates the polarization function. The Ce valence-polarization basis set is then othogonalized to κ_c's constructed from a $(1s)^2...(5s)^2(4p)^6(4d)^{10}$ Cd-like core, which is itself assembled from [(13)3322/(10)32,933/83] pGTFs for s_+, p_-, p_+, and $d_\pm$; in this, $1s_+$, $2s_+$, ..., and $5s_+$ are respectively expanded by 13, three, three, two, and two pGTFs. The F valence basis functions including the two $d_\pm$ type polarization functions[25] are (111/41111/1*1*). The basis functions for the He-like core are composed of 1*s*-like cGTF composed of nine primitives, abbreviated to (9).

The characteristics of RFCA give almost exact atomic and molecular total energies (TE) and spinor energies when it is used in a DFR calculation, which is abbreviated as RFCA-DFR. For example, TE and spinor energies for $4f_-$, $5d_-$, and $6s_+$ for Ce with configuration $[Xe](6s)^2(e_{3/2}{:}5d_-)^1(e_{5/2}{:}4f_-)^1$ based on RFCA-DFR, where the average configuration is used,[27] are

TABLE 1: Calculated Spectroscopic Constants of the Low-Lying States and Upper State of the Red-Degraded Band[a]

no.	configuration	spinor type	Ω	R_e (a.u.)	D_e (eV)	ω_e (cm^{-1})	ν (1-0) (cm^{-1})	T_0 (eV)
1	(5200-aa$\underline{a}$0)[b]	$(6s_+)(5d_-)(4f_-)$	3.5	3.938	5.78	542	539	0.000
		$(6s)(5d)(4f)$	3.5[c]	3.871[c]	6.03 ± 0.44[d]		544[c]	
2	(5200-a(aa)00)	$(6s_+)[(5d_-)(4f_-)]$	2.5	3.922	5.58	538	535	0.195
3	(6200-00a0)	$(6s_+)^2(4f_-)$	2.5	3.825	5.49	580	576	0.290
4	(5200-(a$\underline{a}$)a00)	$[(6s_+)(4f_-)](5d_-)$	1.5	3.933	5.48	534	531	0.295
5	(5200-a$\underline{a}$a0)[b]	$(6s_+)(5d_-)(4f_-)$	4.5	3.940	5.46	536	533	0.319
		$(6s)(5d)(4f)$	4.5[c]	3.868[c]			540 ± 20[c]	0.087[c]
6	(5200-(aa)a00)	$[(6s_+)(4f_-)](5d_-)$	0.5	3.935	5.43	533	530	0.345
7	(5200-a(a$\underline{a}$)00)	$(6s_+)[(5d_-)(4f_-)]$	0.5	3.917	5.39	538	534	0.386
8	(6200-0a$\overline{0}$0)	$(6s_+)^2(4f_-)$	1.5	3.811	5.38	579	576	0.397
9	(5200-a0a$\underline{a}$)	$(6s_+)(5d_+)(4f_+)$	6.5	3.915	5.38	545	542	0.400
10	(5200-$\underline{a}$(a$\overline{a}$)00)[b]	$(6s_+)[(5d_-)(4f_-)]$	3.5	3.920	5.26	534	530	0.518
		$(6s)(5d)(4f)$	(3.5)[c]					0.186 ± 0.002[c]
11	(5200-0aa$\underline{a}$)[b]	$(5d_+)^2(4f_-)$	4.5	3.994	3.58	479	475	2.197
		$(6p)(5d)(4f)$	4.5[c]	3.916[e]			474 ± 20[e]	2.181[e]

[a] Ref 33. The CI total energy for the ground state of CeF at R_e is −8961.209794 a.u. [b] Experimental data are shown in lower rows. [c] Ref 10. The Ω value in parentheses is speculative. [d] Ref 35. [e] Ref 8.

TABLE 2: Spinor Energies and GAOPs of CeF at Equilibrium Nuclear Distances[a]

			Ce						F			
	e	energy	*s*	*p*	*d*	*f*	*g*	total	*s*	*p*	*d*	total
					(5200-1110)							
ionic closed-shell	1/2	−1.50366	0.00	0.08	0.01	0.00	0.00	0.09	1.89	0.01	0.00	1.91
	1/2	−1.13977	0.00	1.93	0.00	0.00	0.00	1.94	0.04	0.02	0.00	0.06
	1/2	−1.02981	0.00	1.87	0.00	0.00	0.00	1.87	0.05	0.08	0.00	0.13
	3/2	−0.99476		1.99	0.00	0.00	0.00	1.99		0.01	0.00	0.01
	1/2	−0.57756	0.00	0.02	0.06	0.02	0.00	0.10	0.00	1.90	0.00	1.90
	1/2	−0.57630	0.00	0.10	0.11	0.02	0.00	0.23	0.00	1.77	0.00	1.77
	3/2	−0.57570		0.02	0.05	0.02	0.00	0.09		1.91	0.00	1.91
	total		0.01	6.01	0.22	0.06	0.00	6.30	1.99	5.71	0.01	7.70
valence-shell	5/2	−0.50349			0.00	1.00[b]	0.00	1.00			0.00	0.00
	3/2	−0.22221		0.00	1.00[b]	0.00	0.00	1.00		0.00	0.00	0.00
	1/2	−0.18564	0.85	0.14	0.02	0.00	0.00	1.00	0.00	0.00	0.00	0.00
	total		0.85	0.14	1.01	1.00	0.00	3.00	0.00	0.00	0.00	0.00
total			0.86	6.15	1.24	1.06	0.00	9.30[c]	1.98	5.70	0.01	7.70
					(5200-1200)							
ionic closed-shell			0.01	6.01	0.23	0.06	0.00	6.31	1.98	5.70	0.01	7.69
valence-shell			0.85	0.13	1.02	1.00	0.00	3.00	0.00	0.00	0.00	0.00
total			0.86	6.14	1.25	1.06	0.00	9.31[c]	1.98	5.70	0.01	7.69
					(6200-0010)							
ionic closed-shell[d]			0.00	6.01	0.26	0.07	0.00	6.35	1.99	5.65	0.01	7.65
valence-shell[d]			1.75	0.10	0.15	1.00	0.00	3.00	0.00	0.00	0.00	0.00
total			1.75	6.11	0.42	1.07	0.00	9.35[c]	1.99	5.66	0.01	7.65
					(5200-0111)							
ionic closed-shell			0.01	6.01	0.21	0.06	0.00	6.28	1.98	5.73	0.01	7.72
valence-shell			0.00	0.30	1.68	1.02	0.00	3.00	0.00	0.00	0.00	0.00
total			0.01	6.31	1.88	1.08	0.00	9.28[c]	1.98	5.73	0.01	7.72

[a] GAOPs are shown for 5200-1110, 5200-1200, 6200-0010, and 5200-0111 at the CI equilibrium distance (R_e) of (5200-aa$\underline{a}$0), [5200-a(aa)00], (6200-00a0), and (5200-0aa$\underline{a}$). The nuclear distances of these four states are, respectively, 3.938, 3.922, 3.835, and 3.994 a.u. These R_e values differ slightly from those for other symmetry states; for example, R_e of (5200-a$\underline{a}$a0) with $\Omega = 4.5$ is 3.940 a.u. The differences between the GAOPs of (5200-1110) of (5200-aa$\underline{a}$0) and (5200-a$\underline{a}$a0) states are smaller than 0.001. We therefore give GAOPs of (5200-1110) at R_e of (5200-aa$\underline{a}$0) as typical. The same argument holds for other configurations. The weights of the main configurations in the CI calculations for these states are 0.90−0.91. [b] The GAOP of the f_- component for $e_{5/2}(4f_-)$ is 0.99, and the GAOP of the d_- component for $e_{3/2}(5d_-)$ is 0.88. [c] The Ce atom has 10 valence electrons. The atomic charges of Ce are +0.70, +0.69, +0.65, and +0.72 for (5200-1110), (5200-1200), (6200-0010), and (5200-0111), respectively. [d] The entry "ionic closed-shell" gives a summation of GAOPs over the three Ce 5*p*- and F 2*s*- and 2*p*-like spinors. The entry "valence-shell" refers to a summation of GAOPs over the other spinors, Ce 4*f*-, 5*d*-, and 6*s*-like spinors. All of the "ionic closed-shell" spinor energies are lower than those for "valence-shell".

−8861.081123, −0.54231, −0.24515, and −0.18178 a.u., whereas those for all electron DFR[28] are −8861.083456, −0.54675, −0.24516, and −0.18179 a.u.

2.2. CI Calculations. As a preamble, we explain our notation for electron configurations. (*pqrs-ijkl*) is an abbreviation for valence electron configurations. The sequences before and after the dash "-" denote the electron occupation of closed and open shells of the respective symmetries of $e_{1/2}$, $e_{3/2}$, $e_{5/2}$, and $e_{7/2}$. The *i*, *j*, *k*, and *l* are either "a" or "$\underline{a}$". The "$\underline{a}$" indicates the Kramer's partners of "a", which stands for +1/2, −3/2, +5/2, −7/2, etc. For example, 5200-a$\underline{a}$a0 indicates that $e_{1/2}$, $e_{3/2}$, $e_{5/2}$, and $e_{7/2}$ symmetries have five, two, zero, and zero closed shells and have one, one, and one open shells with angular momentum, 1/2, 3/2, and 5/2, respectively. If there are two open shell electrons in one symmetry, we use a symbol such as (i, (j_1, j_2), k, l).

Before the CI calculations, we performed DFR calculations. We considered configurations distributing three electrons into four open shells; they are 5200-1110, 5200-1101, 5200-1011, and 5200-0111. Additionally, we treated 5200-3000, 5200-2100, 5200-1200, and 5200-2010 to investigate low-lying states arising from $(4f_-)^1(5d_-)^1(6s_+)^1$ and $(4f_-)^2(6s_+)^1$ types. We further considered 6200-1000, 6200-0100, 6200-0010, and 6200-0001 to investigate $(4f)^1(6s)^2$ type states.

The five $e_{1/2}$ closed shells are composed approximately of Ce $(5p_-)^2$, Ce $(5p_+)^2$, F $(2s_+)^2$, F $(2p_-)^2$, and F $(2p_+)^2$ and the two $e_{3/2}$ of Ce $(5p_+)^2$ and F $(2p_+)^2$. In DFR, we used the average configuration[27] and RFCA, as explained in the previous section.[21]

We performed single-reference SDCI calculations under the no virtual pair approximation.[29−32] In the $C_{\infty v}$ double group, any single determinant belongs to a particular representation of e_λ and forms a configuration state function (CSF). We considered electron correlations among 17 electrons of Ce $(5p)^6$-$(4f)^1(5d)^n(6s)^m$ ($n + m = 2$) and F $(2s)^2(2p)^6$. We performed SDCI from the reference function as stated before; the excitations to all of the half occupied and all of the virtual spinors were considered. The dimension of CI is between 400000 and 450000. To obtain excitation energies of T_0 and spectroscopic constants, we calculated the CI total energies for seven internuclear distances, 2.7, 3.2, 3.7, 4.2, 4.7, 5.2, and 6.0 a.u. The spectroscopic constants were evaluated by fitting a Morse potential function to the calculated points. The dissociation limit was assumed to be the isolated Ce and F atoms under the molecular symmetry $C_{\infty v}$.[33] The electron configurations and CeF bonding were investigated by using Mulliken population analysis.[34]

3. Results and Disscussion

3.1. Excitation Energies and Spectroscopic Constants for the Lower CeF States. Table 1 shows the calculated spectroscopic constants of the ground state, several selected low-lying excited states, and the state near the red-degraded band, together

TABLE 3: Spectroscopic Constants Calculated for the States with T_0 < 2.7 eV[a]

no.	configuration	character[b]	Ω	R_e (a.u.)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	T_0 (eV)
	$(4f)^1(6s)^2$ type						
1	(6200-00a0)	$(1/2{:}s_+)(-1/2{:}s_+)(5/2{:}f_-)$	2.5	3.825	579.5	1.90	0.290
2	(6200-0a00)	$(1/2{:}s_+)(-1/2{:}s_+)(-3/2{:}f_-)$	1.5	3.811	579.4	1.93	0.397
3	(6200-a000)	$(1/2{:}s_+)(-1/2{:}s_+)(1/2{:}f_-)$	0.5	3.822	576.9	1.96	0.513
4	(6200-000a)	$(1/2{:}s_+)(-1/2{:}s_+)(-7/2{:}f_+)$	3.5	3.813	584.7	2.03	0.559
	minimum			3.811	576.9	1.90	0.290
	maximum			3.825	584.7	2.03	0.559
	average			3.818	580.4	1.96	0.435
	$(4f)^1(5d)^1(6s)^1$-type	without an $e_{1/2}(5d_-)$ electron					
1	(5200-aa$\underline{\text{a}}$0)	$(1/2{:}s_+)(-3/2{:}d_-)(-5/2{:}f_-)$	3.5	3.938	542.0	1.58	0.000
4	(5200-a$\underline{\text{a}}$a0)	$(1/2{:}s_+)(3/2{:}d_-)(5/2{:}f_-)$	4.5	3.940	535.9	1.63	0.319
8	(5200-$\underline{\text{a}}$(aa)00)	$(-1/2{:}s_-)(-3/2{:}d_-)(-3/2{:}f_-)$	3.5	3.920	534.0	1.68	0.518
9	(5200-aaa0)	$(1/2{:}s_+)(-3/2{:}d_-)(5/2{:}f_-)$	1.5	3.950	520.8	1.61	0.545
10	(5200-(aa)$\underline{\text{a}}$00)	$(1/2{:}s_+)(3/2{:}d_-)(1/2{:}f_-)$	2.5	3.930	529.8	1.69	0.628
11	(5200-($\underline{\text{a}}$a)a00)	$(-1/2{:}s_+)(-3/2{:}d_-)(1/2{:}f_-)$	1.5	3.930	529.4	1.70	0.665
12	(5200-a($\underline{\text{a}}$a)00)	$(1/2{:}s_+)(3/2{:}d_-)(-3/2{:}f_-)$	0.5	3.915	533.4	1.73	0.691
13	(5200-aa0$\underline{\text{a}}$)	$(1/2{:}s_+)(-3/2{:}d_-)(7/2{:}f_+)$	2.5	3.894	549.0	1.85	0.721
16	(5200-$\underline{\text{a}}$aa0)	$(-1/2{:}s_+)(-3/2{:}d_-)(5/2{:}f_-)$	0.5	3.911	533.1	1.79	0.855
19	(5200-$\underline{\text{a}}$a0a)	$(-1/2{:}s_+)(-3/2{:}d_-)(-7/2{:}f_+)$	5.5	3.909	533.9	1.91	1.142
20	(5200-$\underline{\text{a}}$0aa)	$(-1/2{:}s_+)(5/2{:}d_+)(-7/2{:}f_+)$	1.5	3.879	543.6	2.04	1.280
	minimum			3.879	520.8	1.58	0.000
	maximum			3.950	549.0	2.04	1.280
	average			3.916	537.3	1.75	0.630
		with an $e_{1/2}(5d_-)$ electron					
1	(5200-(a$\underline{\text{a}}$)0a0)	$(-1/2{:}s_+)(1/2{:}d_-)(5/2{:}f_-)$	2.5	3.976	512.8	1.63	0.762
2	(5200-($\underline{\text{a}}$a)0a0)	$(1/2{:}s_+)(-1/2{:}d_-)(5/2{:}f_-)$	2.5	3.973	512.4	1.64	0.807
3	(5200-(aa$\underline{\text{a}}$)000)	$(-1/2{:}s_+)(1/2{:}d_-)(1/2{:}f_-)$	0.5	3.983	504.9	1.65	0.993
4	(5200-(a$\underline{\text{a}}$a)000)	$(1/2{:}s_+)(-1/2{:}d_-)(1/2{:}f_-)$	0.5	3.958	510.7	1.74	1.132
5	(5200-(aa)0a0)	$(1/2{:}s_+)(1/2{:}d_-)(5/2{:}f_-)$	3.5	4.019	494.7	1.65	1.188
6	(5200-(aa)0$\underline{\text{a}}$0)	$(1/2{:}s_+)(1/2{:}d_-)(-5/2{:}f_-)$	1.5	4.018	493.8	1.66	1.225
7	(5200-(aaa)000)	$(1/2{:}s_+)(1/2{:}d_-)(1/2{:}f_-)$	1.5	4.043	479.6	1.65	1.466
8	(5200-($\underline{\text{a}}$aa)000)	$(1/2{:}s_+)(1/2{:}d_-)(-1/2{:}f_-)$	0.5	4.016	485.1	1.74	1.587
	minimum			3.958	479.6	1.63	0.762
	maximum			4.043	512.8	1.74	1.587
	average			3.998	499.3	1.67	1.151
	all $(4f)^1(5d)^1(6s)^1$-type	minimum		3.879	479.6	1.58	0.000
		maximum		4.043	549.0	2.04	1.587
		average		3.940	526.4	1.72	0.777
	$(4f)^1(5d)^2$-type						
1	(5200-0a$\underline{\text{a}}$a)	$(-3/2{:}d_+)(-5/2{:}d_+)(-7/2{:}f_+)$	7.5	4.041	476.0	1.72	1.694
2	(5200-0aa$\underline{\text{a}}$)	$(-3/2{:}d_+)(5/2{:}d_+)(7/2{:}f_+)$	4.5	3.994	478.8	1.99	2.197
3	(5200−0a$\underline{\text{a}}$a)	$(3/2{:}d_+)(5/2{:}d_+)(-7/2{:}f_+)$	0.5	4.008	473.0	2.00	2.301
4	(5200-0aaa)	$(-3/2{:}d_+)(5/2{:}d_+)(-7/2{:}f_+)$	2.5	3.982	471.1	2.22	2.671
	minimum			3.982	471.1	1.72	1.694
	maximum			4.041	478.8	2.22	2.671
	average			4.006	474.7	1.98	2.215

[a] The first column indicates the number of state in the respective configurations. In $(4f)^1(5d)^1(6s)^1$, we have not shown all of the states, save the space. [b] Letters in parentheses denote the occupied valence spinor types. The notations adopted here are abbreviated; for example, $(1/2{:}s_+)$ and $(-5/2{:}d_+)$ mean $e_{1/2}$;1/2($6s_+$) and $e_{5/2}$;−5/2($5d_+$), respectively.

with experimental results. Figure 1 shows calculated potential energy curves. The DFR total energies, the spinor energies, and the gross atomic orbital populations (GAOP) for several important configurations are set out in Table 2. In this table, we use the entry "ionic closed shell" and "valence shell", which, respectively, indicate the ionic core of CeF and the valence electrons not included in the ionic core.

In the ground state, the weight of the main configuration (5200-aa$\underline{\text{a}}$0) in the CI is 0.91, having the atomic-like configuration $(e_{1/2}{:}6s_+)^1(e_{3/2}{:}5d_-)^1(e_{5/2}{:}4f_-)^1$ as suggested from GAOP in Table 2. The weights of main configurations are also found to be 0.90−0.91 for all of the other electronic states discussed below. The absolute value of the projection of the total electronic angular momentum on the molecular axis Ω is 3.5 for the ground state. The equilibrium distance R_e, the dissociation energy D_e, and the 1-0 vibrational transition ν(1-0) are 3.938 a.u., 5.78 eV, and 539 cm^{-1} (see Table 1). The experimental Ω is 3.5, and R_e, D_e, and ν(1-0) are 3.871 a.u.,[10] 6.03 eV,[35] and 544 cm^{-1}.[10] Because we used a single reference CI, the calculated R_e, D_e, and ν(1-0) include the errors caused by a size consistency. However, for example, the error in D_e is around 0.4 eV. The small error arises from the characteristics of ionic compounds where the DFR explains the major part (5.13 eV) of the chemical bonding.

The electron configuration suggested by ligand-field theory is $(4f)^1(5d)^1(6s)^1$, ^4H,[10] which is consistent with the present designation. The calculated spectroscopic constants agree with the experimental values, although the calculated R_e is slightly longer and ν(1-0) is slightly smaller than experimental ones.

The calculated first excitated state is 0.195 eV above the ground state. This state is composed mainly of (5200-a(aa)00), having characteristics of $(e_{1/2}{:}6s_+)^1(e_{3/2}{:}4f_-)^1$ $(e_{3/2}{:}5d_-)^1$ as suggested in Table 2. The Ω is 2.5. All experimentally assigned states including the ground state are determined using emission spectra from the state with Ω = 4.5. This state is not observed, because transitions from the state with Ω = 4.5 are dipole forbidden.

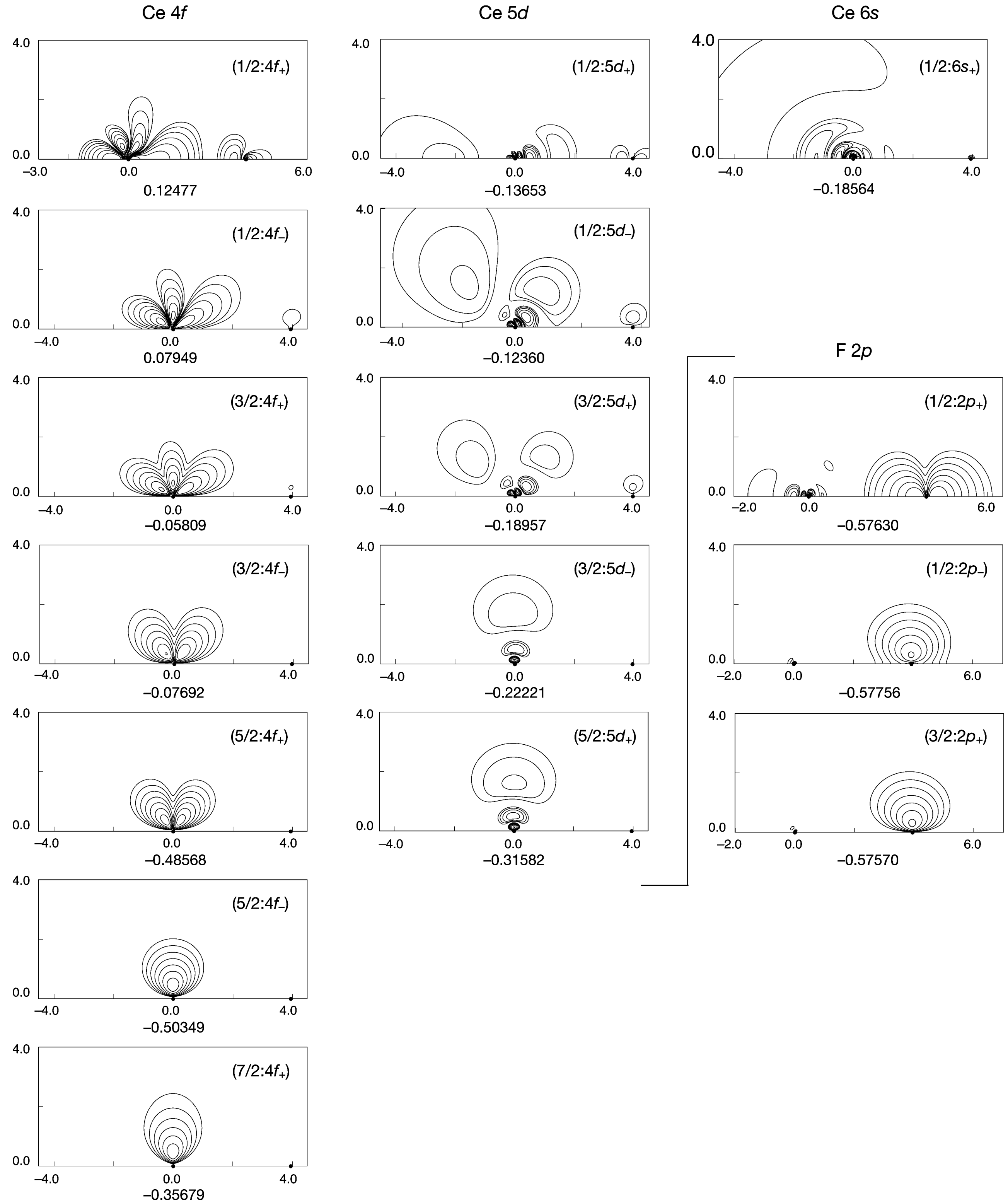

Figure 2. Contour maps of densities of the valence spinors in the ground state, together with the spinor energies. The (λ/2:*function*) means *function* belonging to $e_{\lambda/2}$; for example, (1/2:4f_+) means $e_{1/2}$; 4f_+. The spinors are shown in order of orbital angular momentum about the internuclear axis. Each spinor energy (in a.u.) is shown under the contour map. The horizontal and vertical (z and x) axes are in a.u., respectively. The circles on the z-axis at $z = 0.0$ and 3.938 a.u. indicate the Ce and F nuclei, respectively. The outermost values of the contour line are 0.005 e a.u.$^{-3}$ except those of the $e_{1/2}(5d_-)$ and $e_{1/2}(6s_+)$ spinors, for which the outermost contour lines are 0.00125 e a.u.$^{-3}$. The value of an inner line is twice as large as that of the neighboring outer line.

In contrast to some LnF molecules in which the $(4f)^n(6s)^2$ is the ground state,[16] the $(e_{1/2}{:}6s_+)^2(e_{5/2}{:}4f_-)^1$ state with $\Omega = 2.5$ is the second lowest excited state (i.e., the third state; see Table 1). This state lies 0.290 eV above the ground state. The Ω value of the lowest $(4f)^1(6s)^2$ state agrees with previous theoretical results.[9,13]

In no DFR calculation using (5200-1110), (5200-1101), (5200-1011), and other configurations, we do find a $(4f)^2(6s)^1$ type state, which constitutes the ground state for other LnF molecules, as outlined in the introduction. We cannot therefore perform CI calculations with this as a reference configuration.

Let us discuss the fifth state with $T_0 = 0.319$ eV. This state is composed mainly of (5200-a$\underline{\text{a}}$a0) and has the atomic-like configuration $(e_{1/2}{:}6s_+)^1(e_{3/2}{:}5d_-)^1(e_{5/2}{:}4f_-)^1$ with $\Omega = 4.5$. This corresponds to the observed first excited state with $T_0 = 0.087$ eV. Although the calculated R_e and ν(1-0) values of 3.940 a.u. and 533 cm^{-1} agree with those of experiment, 3.868 a.u. and 540 cm^{-1},[10] the difference in T_0 is a little larger. We believe that this discrepancy arises from the defect that the present calculational scheme does not take into full account core-valence correlation. We are not aware of any theoretical calculations on the $\Omega = 4.5 \leftarrow \Omega = 3.5$ transition. Instead of this, we found $(4f_{7/2})(6s)^2 \leftarrow (4f_{5/2})(6s)^2$ transitions by LFT combined with parameters obtained by density functional theory.[13] The LFT gives 0.268 eV while the present 0.269 eV [see entry $(4f)^1(6s)^2$ in Table 3], indicating that the present calculations have the same reliability as LFT. We, however, feel that further investigations are necessary to confirm the discussion given above. The sixth to ninth calculated states are dipole forbidden transitions.

The tenth state is composed mainly of (5200-$\underline{\text{a}}$(aa)00) and has $(e_{1/2}{:}6s_-)^1(e_{3/2}{:}5d_-)^1(e_{3/2}{:}4f_-)^1$ with $\Omega = 3.5$; it lies 0.518 eV above the ground state. We take this to be the observed second excited state. The calculated T_0 is larger than the experimental one, of 0.186 eV,[10] as for the state at 0.087 eV with $\Omega = 4.5$. The calculated R_e and ν(1-0) are 3.920 a.u. and 530 cm^{-1}; no experimental values are known.

Finally, we discuss the state with $\Omega = 4.5$ observed at 2.181 eV above the ground state. We have two candidates, but one of these at $T_0 = 2.301$ eV has $\Omega = 0.5$ (see Table 3 given in the next subsection). We therefore disregarded this state when considering the experimental state at 2.181 eV. The other calculated state, composed mainly of (5200-0aa$\underline{\text{a}}$), has $(e_{3/2}{:}5d_+)^1(e_{5/2}{:}5d_+)^1(e_{7/2}{:}4f_+)^1$ with $\Omega = 4.5$, and it lies 2.197 eV above the ground state. We assigned this to the upper state of the red-degraded band. The experimental Ω and T_0 are 4.5 and 2.181 eV (5679.4 Å),[8] which agrees with the calculated values. The GAOPs in Table 2 give the electronic configuration of $(4f)^{1.0}(5d)^{1.7}(6p)^{0.3}$. This does not accord with the experimental configuration of $(4f)^1(5d)^1(^3H)(6p)^1$,[10] although the spinor written as $e_{3/2}(5d_+)$ in $(4f)^{1.0}(5d)^{1.7}(6p)^{0.3}$ contains a fraction 0.30 of $6p_+$. The calculated R_e and ν(1-0) values are 3.994 a.u. and 475 cm^{-1}, which agree with the experimental R_e and ν(1-0) of 3.916 a.u. and 474 cm^{-1}.[8]

The calculational results are satisfactory, since the CI calculations gave the same ordering of the energies of the states as experiment; specifically, the lowest state is $(e_{1/2}{:}6s_+)^1(e_{3/2}{:}5d_-)^1(e_{5/2}{:}4f_-)^1$ with $\Omega = 3.5$, the second lowest is $(e_{1/2}{:}6s_+)^1(e_{3/2}{:}5d_-)^1(e_{5/2}{:}4f_-)^1$ with $\Omega = 4.5$, and the third is $(e_{1/2}{:}6s_-)^1(e_{3/2}{:}5d_-)^1(e_{3/2}{:}4f_-)^1$ with $\Omega = 3.5$. The origin of the emissions of 2.181 eV is correctly identified by the present CI calculations.

3.2. Bonding between Ce and F. Table 2 shows that the atomic charges on the Ce and F are approximately $+0.7$ and -0.7 *e*, irrespective of the states (see footnote c). These atomic charges are similar to those of LnF molecules; for example, for the GdF molecule, the GAOPs for Gd are $+0.60 \sim +0.65$.[19] The ionicity of the bonding of CeF is therefore slightly higher than that of GdF.

The entry "valence shell" in Table 2 shows that the valence-shell GAOPs for Ce and F are 3.0 and 0.0, respectively, giving rise to $(4f)^1(5d)^1(6s)^1$ from 5200-1110 and 5200-1200, $(4f)^1(5d)^2$ from 5200-0111, and $(4f)^1(6s)^2$ from 6200-0010. Three valence 6*s*-, 5*d*-, and 4*f*-like electrons move in the field composed of $[\mathrm{Ce}^{4+}(5p)^6\mathrm{F}^-(2p)^6]$. The positively charged Ce^{4+} ion core and the electron cloud at F$^-$ localize the valence electrons at the Ce$^+$.

The ionicity of the CeF bonding in the ground state is incomplete so far as we see the Mulliken populations. We interpret this as 0.3 electrons are transferred from the F$^-$ ion to the Ce^{4+} ion through the 5*d* and 4*f* spinors, which are used to polarize the Ce$^{4+}(5p)^6$ core in the CeF [see ionic closed-shell in entry (5200-1110) of Table 2]. We may thus interpret the valence electron of F$^-$ as one and part of which are lent out to the Ce ion through the polarization spinors. This discussion gives the reasonableness of the formal charge, $+1$ and -1 *e*, for the Ce and F ions, respectively.

Contour maps of densities of all of the valence and virtual spinors of the ground state are shown in Figure 2. The 5*d*- and 4*f*-like spinors with low energies are strongly localized at the Ce$^+$ ion, whereas the $6s_+$ extends to the opposite side of the F$^-$ ion. The valence electrons in the respective Ce spinors are distributed according to the balances of the attractive potential by the Ce^{4+} core and the repulsive potential provided by the F$^-$ ion.

If we attach two electrons to Ce^{4+}F$^-$, we find that the lowest configuration at $R_e = 3.938$ a.u. has (5200-0110), giving $[\mathrm{Ce}^{2+}(e_{5/2}{:}4f_-)^1(e_{3/2}{:}5d_-)^1\ \mathrm{F}^-(2p)^6]^+$. This indicates that the electrostatic field given by Ce^{4+}F$^-$ is not strong enough to hold two 4*f* electrons; we recall that if the nuclear attraction is very strong as compared to the electron−electron repulsions, 4*s*, 4*p*, 4*d*, and 4*f* would be degenerated. Also, we found $e_{1/2}(6s_+) = -0.17569$ and $e_{1/2}(5d_-) = -0.12481$ a.u., suggesting the electrostatic field in $[\mathrm{Ce}^{2+}(e_{5/2}{:}4f_-)^1(e_{3/2}{:}5d_-)^1\ \mathrm{F}^-(2p)^6]^+$ capture first the 6*s* and the next 5*d* electron; virtual spinor energies in DFR approximately give the electron affinity for the system under consideration. Thus, the molecule CeF is predicted to take $(4f_-)^1(5d_-)^1(6s_+)^1$ rather than $(4f)^1(5d)^2$, which is confirmed with the DFR calculation on the neutral molecule having GAOPs near to $(4f_-)^1(5d_-)^1(6s_+)^1$ as was discussed (see Table 1). The model discussed above is parallel to those of LaF$^+$ and LaF, which will be discussed elsewhere.[36]

We now discuss the influence of excitations from 6*s* to 5*d* on the bond distance. Figure 2 shows that the 5*d* charge cloud between the Ce and the F centers are denser than $6s_+$. We can therefore expect that the increase in the occupation numbers of the *d* spinors will give a greater R_e, since the repulsions between Ce 5*d* and F 2*p* become stronger. We actually see from Table 3 that R_e increases in the order of $(4f)^1(6s)^2 < (4f)^1(5d)^1(6s)^1 < (4f)^1(5d)^2$. Table 3 also shows that the electron occupancy of the $e_{1/2}(5d_-)$ spinor increases R_e in the $(4f)^1(5d)^1(6s)^1$ states by their averages, because the repulsion between $e_{1/2}(5d_-)$ and F 2*p* is larger than that between $e_{3/2}(5d_-)$ and F 2*p*. The R_e values of $(4f)^1(e_{1/2}{:}5d_-)^1(6s)^1$ states are close to those of the $(4f)^1(5d)^2$ states. The electron occupancy of any 4*f* spinors has very little effect on R_e as compared to 5*d* spinors, since the 4*f* spinors are tightly bound around the Ce nucleus.

4. Conclusion

We have studied the electronic structures of the CeF molecule using the frozen-core four-component relativistic configuration interaction method. The Ω, R_e, and ν(1-0) values for the ground and excited states fairly agree with experiment. The electron configurations of the ground and some low-lying states are $(4f)^1(5d)^1(6s)^1$, in contrast to ordinary LnF molecules having $(4f)^{n-1}(6s)^2$ and $(4f)^n(6s)^1$. The state observed experimentally at 5679.4 Å (2.181 eV) is identified as $(4f)^{1.0}(5d)^{1.7}(6p)^{0.3}$.

The bonding between the Ce and the F is highly ionic. The 4*f*, 5*d*, and 6*s* valence electrons are localized at Ce, because they are attracted by the Ce^{4+} ion core and excluded from the bonding region as a result of the electronic cloud of the fluoride anion. Localization of the 4*f*, 5*d*, and 6*s* electrons at Ce suggests that LFT is a good approximation in studying the electronic structures of the LnF molecules.

The 5*d* → 6*s* excitation tightens the ionic bond, because the 6*s* electron has little density in the bonding region, increasing the attraction between the Ce^{+} and the F^{-} ions. The bonding in the ground and excited states of the CeF molecule was significantly affected by the 6*s* and 5*d* electron densities between the Ce and the F.

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