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REGULAR ARTICLE

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On the bond length change upon $4f^1 \rightarrow 5d^1$ excitations in eightfold coordination: CaF$_2$:Ce^{3+} cubic defects

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Abstract The bond lengths of $4f^1$ and $5d^1$ electronic states of cubic $(\mathrm{CeF_8})^{5-}$ defects in fluorite have been calculated using quantum mechanical embedding, spin-free relativistic Hamiltonian, and dynamic electron correlation through second-order perturbation theory. The results predict the bond length between Ce and the surrounding eight F to shorten upon $4f^1 \rightarrow 5d^1$ excitation. This result coincides with previous findings for lanthanide and actinide ions in sixfold octahedral complexes where the ligand field splitting of the $5d$ ($6d$) orbitals is inverted with respect to the eightfold cubic field splitting. Altogether, the results of sixfold and eightfold coordination indicate that the bond shrinkage experienced upon $4f^n$ to $4f^{n-1}5d^1$ excitations ($5f^n$ to $5f^{n-1}6d^1$ in the actinides) seems to be a general result of f-element complexes. These theoretical results contradict a widespread assumption according to which the bond length increases upon $f \rightarrow d$ excitation and, therefore, experimental measurements of the sign of the bond length distortion that either validate or refute the quantum chemical predictions are most desirable.

1 Introduction

It is known that the radial extent of $4f$ orbitals of the lanthanide ions is much smaller than that of the $5d$ orbitals. This can be illustrated by the expected value of r resulting from numerical Cowan-Griffin Hartree-Fock calculations in Ce^{3+}: $\langle r\rangle_{4f} = 0.540\,\text{Å}$, $\langle r\rangle_{5d} = 1.199\,\text{Å}$. The same is true for the actinide (An) ions where the same type of calculations lead to $\langle r\rangle_{5f} = 0.725\,\text{Å}$ and $\langle r\rangle_{6d} = 1.247\,\text{Å}$ in isoelectronic Pa^{4+}. Probably associated with the different radial extents, it is often assumed in the literature that $4f^n \rightarrow 4f^{n-1}5d^1$ and $5f^n \rightarrow 5f^{n-1}6d^1$ excitations enlarge the bond length between the f element and the surrounding ligands in their complexes (see Fig. 2 of Ref. [1] as an example of this assumption). Yet, no experimental proof has been given that supports or rejects this belief. On the one hand, the analyses of the $f^n \longleftrightarrow f^{n-1}d^1$ band shapes lead to the square of the bond length shift $[\Delta R_e(f^n \rightarrow f^{n-1}d^1)]^2$, and, therefore, the actual sign remains hidden; on the other hand, direct measurements of the bond length in the excited state are very difficult; for example, they may require the performance of EXAFS experiments with an additional laser that produces and maintains the $f^{n-1}d^1$ excited state population. No experiments of this kind, leading to the shift $\Delta R_e(f^n \rightarrow f^{n-1}d^1)$ have been reported, to our knowledge.

From the theoretical side, quantum chemical studies of the bond lengths of Ln and An ion complexes in gas phase, liquid solution, and halide crystals have shown that $f^n \rightarrow f^{n-1}d^1$ excitations actually shorten the bond length between the f-element and the ligands in sixfold octahedral coordination (Refs. [2,3], and references therein), in contradiction to the assumption described earlier. In effect, the $4f^1 \rightarrow 5d(t_{2g})^1$ excitation of $(\mathrm{Ce}X_6)^{3-}$ (X=F, Cl, Br) in elpasolites shortens the Ce–X. distance by: (F) 0.009, (Cl) 0.042, and (Br) 0.046 Å. Analogous results are obtained for the same complexes in acetonitrile solution and in gas phase [3].

Calculations that include spin-orbit effects and dynamic electron correlation in $(\mathrm{AnCl_6})^{q-}$ embedded clusters have shown that the shrinkage of bond length upon $f \rightarrow d$ excitation is neither due to dynamic electron correlation nor due to spin-orbit coupling, since it is already visible at lower levels of theory, namely, using a spin-free relativistic Hamiltonian and a CASSCF wavefunction where the MOs corresponding to the $(fd)^n$ open-shells define the active space [4,5]. This means that the bond length shift is associated with bonding interactions, such as orbital mixing, charge transfer, and ligand field splitting. The role of these interactions has been studied in constrained space orbital variation [6,7] calculations in Ce^{3+}, Pr^{3+}, Pa^{4+}, and U^{4+} defects in chloride

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hosts, where the Ln (An) ions have sixfold octahedral coordination, to analyze the bonding interactions [2]. A simple model of the interactions emerged from these calculations, which is as follows: the inner Ln (An) f^n open-shell electrons are shielded from the ligands by the outer Ln $5p^6$ (An $6p^6$) closed-shell electrons, whose interaction with the ligands determines the bond distance in the states of f^n configuration. Instead, in $f^{n-1}d^1$ configurations, one electron has crossed the $5p^6$ ($6p^6$) barrier and is exposed to covalent interactions with the ligands, leaving a $4f$ ($5f$) hole behind, both effects contributing to shortening of the bond length. Finally, a large $d(t_{2g})$–$d(e_g)$ octahedral ligand field splitting, which is enhanced by covalency, lowers the $f^{n-1}d(t_{2g})^1$ bond lengths clearly below the f^n ones, and raises the $f^{n-1}d(e_g)^1$ ones clearly above them [2].

The shortening of the bond length upon $f \rightarrow d$ excitation has only been studied in sixfold octahedral coordination and the question remains of whether the same result will be obtained in different coordinations, in particular, if the ligand field splitting of the $4d(5d)$ antibonding orbitals is reversed, as it is the case of eightfold cubic coordination, where the $d(e_g)$ orbitals, pointing towards the center of the cube faces are stabilized by the ligand field, whereas the $d(t_{2g})$, pointing towards the center of the cube edges, are destabilized relative to their d baricenter. The purpose of the work we present here is to study the bond length shifts on an eightfold cubic model system by means of ab initio calculations. The results of this work, together with those obtained in sixfold octahedral coordination make the predicted shrinkage of bond length upon $f \rightarrow d$ excitation more general.

Ce^{3+} cubic centres have been recently detected experimentally [8]. Interconfigurational $4f \leftrightarrow 5d$ VUV absorption and luminescence, intra-$4f^1$ IR absorption and X-band EPR measurements on CaF_2:Ce^{3+} co-doped with Na^+ and Li^+ ions, have been reported [8]. The authors have detected cubic centres that are readily observable by their infrared transitions. The infrared lines corresponding to the cubic centres are identical for Li^+ and Na^+ doping and reveal non-local charge compensation by distant Li^+ or Na^+ ions, a fact that makes this material a perfect model system for the study of an f element ion in eightfold cubic coordination.

Since the work we present here is a structural study of the CaF_2:Ce^{3+} cubic defect aimed at revealing the bond length shifts that follow $f^1 \rightarrow d(e_g)^1$ and $f^1 \rightarrow d(t_{2g})^1$ excitations, the calculations include embedding effects associated with the surrounding fluorite host, scalar relativistic effects, and electron correlation effects. Spin-orbit coupling would affect the electronic transition energy values, but not the structural parameters, and, therefore, has been safely excluded from the calculations, the details of which are presented in Sect. 2. In Sect. 3 the results are described and discussed. The conclusions are presented in Sect. 4.

2 Details of the calculations

Since the charge compensation of the cubic defects is non-local, the Ce^{3+}, Li^+/Na^+ co-doped CaF_2 materials can be modeled as CaF_2:$(CeF_8)^{5-}$ where the Ce^{3+} impurity ion substitutes for one Ca^{2+} ion and is surrounded by eight fluorines forming a perfect cube in a cubic site. The purpose of this study is to obtain the potential energy surfaces of the $4f^1$ ($^2T_{1u}$, $^2T_{2u}$, $^2A_{2u}$) and $5d^1$ (^2E_g and $^2T_{2g}$) manifolds of the cubic $(CeF_8)^{5-}$ embedded in CaF_2, along the a_{1g} breathing mode of the CeF_8 unit, so as to derive their respective spectroscopic constants: bond lengths, R_e, totally symmetric vibrational frequencies, $\bar{\nu}_{a_{1g}}$, and minimum-to-minimum transition energies, T_e. In order to model the interactions between the $(CeF_8)^{5-}$ unit and the surrounding fluorite host we used the ab initio model potential (AIMP) embedding [9, 10] whose particular parameters for CaF_2 (a_0 = 5.462 94 Å) [11] have been obtained elsewhere [12]. The AIMP method was also used to reduce the calculations to the cluster valence electrons and to incorporate spin-free relativistic effects associated with the Cowan-Griffin approximation [13]. We used the [Kr] core AIMP and $(14s10p10d8f3g)$ valence basis set [14] contracted as $[6s5p6d4f1g]$ for Ce, which includes $(3g)/[1g]$ polarization functions obtained by maximum radial overlap with the $4f$ atomic orbitals, and the [He] core AIMP and $(5s6p1d)$ valence basis set [15] contracted as $[3s4p1d]$ for F, which includes $1p$ diffuse function for anions [16] and $1d$ polarization function [17]. f functions are known to be needed to correlate d open-shells in transition metal complexes in solids (see Ref. [10] and references therein); it is expected that the $(8f)[4f]$ basis of Ce^{3+} should fulfill this role for the $5d$ orbitals here. In order to include dynamic electron correlation, SCF calculations were performed on the $4f^1$ and $5d^1$ electronic states mentioned previously and were used as reference for second-order perturbation calculations (CASPT2) where 73 valence electrons were correlated that occupy molecular orbitals with main character Ce $5s, 5p, 4f/5d$ and F $2s, 2p$ [18,19]. All the calculations were done using the MOLCAS package [20].

3 Results and discussion

The results of the calculations are included in Table 1 and Fig. 1. The minimum-to-minimum transition energies, although approximate due to the lack of spin-orbit coupling, are accurate enough so as to confirm that the ligand field effect on the $5d^1$ states is reversed relative to that produced by sixfold octahedral coordination, being $E(^2E_g) < E(^2T_{2g})$. The equilibrium distances show that the Ce–F bond length shortens upon $4f^1 \rightarrow 5d^1$ excitation by some 0.019 Å in this inverted field showcase. This result makes the predictions obtained in octahedral coordination more general.

The simple model of interactions suggested by the constrained space orbital variation calculations to explain the bond length shifts from f^n to $f^{n-1}d^1$ configurations in octahedral complexes described elsewhere [2] applies here as well, as we comment next. The values of the equilibrium distances and vibrational frequencies of the f^1 states ($^2T_{1u}$, $^2T_{2u}$, $^2A_{2u}$) show parallel potential energy surfaces with bond length 2.30 Å (Table 1, Fig. 1), being the largest shift 0.006 Å

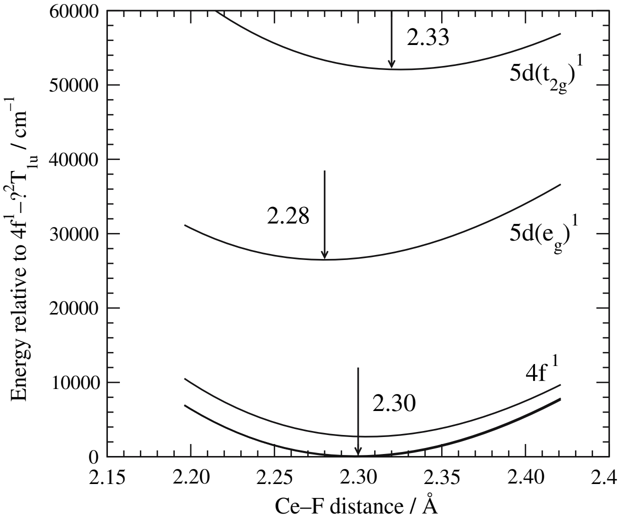

Fig. 1 Potential energy surfaces of $4f^1 -^2 T_{1u}$, $^2T_{2u}$, $^2A_{2u}$, $5d\,(e_g)^1 -^2 E_g$, and $5d(t_{2g})^1 -^2 T_{2g}$ electronic states of cubic CaF$_2$:Ce^{3+} defects. The *arrows* indicate the calculated bond length values

Table 1 Spectroscopic constants of the $4f^1$ and $5d^1$ electronic states of CaF$_2$:(CeF$_8$)$^{5-}$ cubic defects [Ce−F bond distance R_e(Å), breathing mode vibrational frequency, $\bar{\nu}_{a_{1g}}$ (cm^{-1}), and minimum-to-minimum energy T_e (cm^{-1})] as calculated with the spin-free relativistic Cowan-Griffin AIMP embedded cluster Hamiltonian. The calculations include correlation of 73 electrons associated with Ce $5s$, $5p$, $4f$, $5d$, and F $2s$, $2p$ orbitals. Spin-orbit coupling is not included

	CASPT2			
	R_e	$\bar{\nu}_{a_{1g}}$	T_e	$\Delta R_e(^2T_{1u} \rightarrow 5d^1)$
$4f^1$ manifold				
$^2T_{1u}$	2.299	512	0	
$^2T_{2u}$	2.298	512	94	
$^2A_{2u}$	2.305	512	2700	
$5d$ manifold				
$\langle 5d\rangle^a$	2.307		36560	+0.008
^2E_g	2.280	519	26500	−0.019
$^2T_{2g}$	2.325	508	52100	+0.026

[a] Properties of the $5d$ baricenter are given: $R_e(\langle 5d\rangle) = [2\times R_e(^2E_g) + 3\times R_e(^2T_{2g})]/5$; $T_e(\langle 5d\rangle) = [2\times T_e(^2E_g) + 3\times T_e(^2T_{2g})]/5$

[corresponding to the non-bonding $4f(a_{2u})^1 -^2 A_{2u}$ state]. The negligible bond length shifts within the f^1 manifold show the very low ligand field effects on the molecular orbitals of main character Ce $4f$, associated with their short radial extent and the effective shielding of the Ce $5p$ shell. This suggests that the equilibrium distance of the $4f^1$ states is determined by the interactions between the Ce $5p^6$ closed-shell and the ligands and, therefore, by the radial extent of the $5p^6$ shell that can be roughly estimated by its radial expectation value $\langle r\rangle_{5p}$. As one electron is excited to the $5d^1$ shell, it becomes exposed to the ligand's effects and, more important, a $4f$ hole is created that favors charge transfer from the ligands. Consequently, the bond length of the $5d^1$ baricenter state (a ficticiuous state where ligand field effects on the d shell are excluded by estimating its properties as weighted averages over the real ligand field components) should be shorter than that expected from the radial extent of the $5d^1$ orbitals; rather, it could be roughly estimated as: $\langle r\rangle_{5p^6 5d^1} = [6\langle r\rangle_{5p} + \langle r\rangle_{6d}]/7$, and the difference $\langle r\rangle_{5p^6 5d^1} - \langle r\rangle_{5p^6} = 0.019$ Å for Ce^{3+} free ion, could be seen as an upperbound to the $4f^1 \rightarrow 5d^1$ bond length change in the complex. The results in Table 1 show that the bond length shift of the $5d$ baricenter relative to the ground state is $\Delta R_e(^2T_{1u} \rightarrow \langle 5d\rangle)$ = 0.008 Å, which is smaller than the 0.019 Å upperbound estimate and shows the effects of the $5d$ exposure to covalent interactions including charge transfer from the ligands to the f hole (the extra electronic charge on the f basis functions obtained by Mulliken population analyses of the SCF wavefunctions is some 15% larger in the $5d^1$ states than in the $4f^1$ states; this extra charge transfer to the f functions becomes 21% larger in the $5d^1$ states than in the $4f^1$ ones when the Mulliken population is done using the natural orbitals obtained from the second-order perturbation calculations). The final effect comes from the ligand field splitting of the $5d^1$ baricenter state. This effect reduces notably the bond length of the more stable d component, which in eightfold cubic coordination is the $d(e_g)^1 -^2 E_g$, pointing towards the center of the (CeF$_8$)$^{5-}$ cube faces, while it increases significantly the bond length of the less stable d component, $d(t_{2g})^1 -^2 T_{2g}$, which points to the center of the edges, more directly towards the ligands, so that the final result is: $\Delta R_e(^2T_{1u} \rightarrow^2 E_g) = -0.019$ Å. It should be noted that if the Ce^{3+} free ion expected values $\langle r\rangle_{4f} = 0.540$ Å and $\langle r\rangle_{5d} = 1.199$ Å were used to roughly estimate the $f \rightarrow d$ bond length shift, the upper limit set for the bond length change of the $5d^1$ baricenter would be unacceptably larger: some 0.659 Å and would lead to predictions of too long equilibrium distances of both ligand field components and, hence, bond length increase upon $f \rightarrow d$ excitation, a fact that ab initio calculations do not support.

4 Conclusions

We present a structural study of the recently detected cubic (CeF$_8$)$^{5-}$ defects in CaF$_2$:Ce^{3+} crystals co-doped with Li$^+$ or Na$^+$. The calculations include quantum mechanical embedding effects, scalar relativistic effects, and valence electron correlation through second-order perturbation theory within the (CeF$_8$)$^{5-}$ embedded cluster. Their results reveal that the bond length between the Ce^{3+} impurity and the eight surrounding fluorine ligands shortens by 0.019 Å upon $4f^1 \rightarrow 5d(e_g)^1$ excitation. This result confirms previous findings in lanthanide and actinide ion complexes in sixfold octahedral coordination in gas phase, acetonitrile solution, and halide crystals and, therefore, points out the shrinkage in bond length as a general result for the $f^n \rightarrow f^{n-1}d^1$ interconfigurational transition. The predicted bond length shrinkage contradicts an extended assumption according to which the bond length increases upon $f^n \rightarrow f^{n-1}d^1$ excitation and, therefore, urge the need for experiments, such as excited state EXAFS, that might confirm or reject the quantum chemical predictions.

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References

1. Khaidukov NM, Kirm M, Lam SK, Lo D, Mkhov VN, Zimmerer G (2000) Opt Comm 184:183
2. Barandiarán Z, Seijo L (2003) J Chem Phys 119:3785
3. Barandiarán Z, Edelstein NM, Belén Ordejón, Ruipérez F, Seijo L (in press) J Solid State Chem
4. Seijo L, Barandiarán Z (2003) J Chem Phys 118:5335
5. Barandiarán Z, Seijo L (2003) J Chem Phys 118:7439
6. Bagus PS, Hermann K, Bauschlicher CW (1984) J Chem Phys 80:4378
7. Bauschlicher CW, Bagus PS (1984) J Chem Phys 81:5889
8. Yamaga M, Yabashi S, Masui Y, Honda M, Takahashi H, Sakai M, Sarukura N, Wells J-PR, Jones GD (2004) J Lumin 108:307
9. Barandiarán Z, Seijo L (1988) J Chem Phys 89:5739
10. Seijo L, Barandiarán Z (1999) In: Computational chemistry: reviews of current trends, Leszczyński J (Ed.) World Scientific: Singapore vol. 4 pp 55
11. Hayes W (Ed.) (1974) Crystals with the fluorite structure, Clarendon: Oxford
12. Pascual JL, Seijo L (1995) J Chem Phys 102:5368
13. Cowan RD, Griffin DC (1976) J Opt Soc Am 66:1010
14. Seijo L, Barandiarán Z, Ordejón B (2003) Mol Phys 101:73
15. Barandiarán Z, Seijo L (1992) Can J Chem 70:409
16. Dunning TH, Hay PJ (1977) In: Modern theoretical chemistry, Schaefer III HF (Ed.) Plenum:New York
17. Andzelm J, Klobukowski M, Radzio-Andzelm E, Sakai Y, Tatewaki H (1984) Gaussian basis sets for molecular calculations Huzinaga S (Ed.) Elsevier:Amsterdam
18. Andersson K, Malmqvist P-Å, Roos BO, Sadlej AJ, Wolinski K (1990) J Phys Chem 94:5483
19. Andersson K, Malmqvist P-Å, Roos BO (1992) J Chem Phys 96:1218
20. Karlström G, Lindh R, Malmqvist PA, Roos BO, Ryde U, Veryazov V, Widmark PO, Cossi M, Schimmelpfennig B, Neogrady P, Seijo L (2003) Comp Mater Sci 28:22