

# Bond lengths of $4f^1$ and $5d^1$ states of $\text{Ce}^{3+}$ hexahalides

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## Abstract

Ligand and solvent effects on the bond length shift experienced by complexes of lanthanide ions upon  $4f \rightarrow 5d$  excitation, addressed by means of ab initio embedded cluster calculations, are presented on the clusters  $(\text{CeF}_6)^{3-}$ ,  $(\text{CeCl}_6)^{3-}$ , and  $(\text{CeBr}_6)^{3-}$  in solid elpasolites, in liquid acetonitrile and in vacuo. Previous predictions of bond length shortening upon  $4f \rightarrow 5d(t_{2g})$  excitation seem to be general and, in particular, chloride and bromide compounds in liquid solution are predicted to be good candidates for excited-state EXAFS measurements of the distortion signs. A quantitative analysis of contributions to the bond length shifts is presented, which shows the importance of ligand field effects and points out insufficiencies in the Judd–Morrison model proposed to account for  $4f \rightarrow 5d$  transitions in crystals.

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## 1. Introduction

Although the bond lengths between  $f$ -element ions and their ligands have been traditionally assumed to lengthen upon  $4f \rightarrow 5d$  and  $5f \rightarrow 6d$  electronic excitations (see Fig. 2 of Ref. [1] as an example of this assumption), ab initio theoretical studies on lanthanide and actinide impurities in chloride crystals with the  $f$ -element ion in an octahedral sixfold coordination have shown that the bond length is in fact shortened by  $f \rightarrow d(t_{2g})$  excitations and lengthened by  $f \rightarrow d(e_g)$  excitations [2–6]. On the basis of a quantum chemical analysis of interactions [6], the bond length shifts have been

interpreted as originating from two effects: (i) The inner  $f^n$  open-shell is shielded by the outer  $p^6$  closed-shell, whose interaction with the ligands dominates the bond length in the  $f^n$  configuration, but the  $f \rightarrow d$  excitation exposes the  $d$  electron to covalent interactions and leaves an inner  $f$ -hole behind, both effects leading to a shortening of the bond length upon excitation. (ii) A large effective ligand field, which is enhanced by covalency, stabilizes the  $d(t_{2g})$  and destabilizes the  $d(e_g)$  molecular orbitals, which further shortens the bond length in the  $f \rightarrow d(t_{2g})$  excitation and lengthens it in the  $f \rightarrow d(e_g)$  excitation.

The ab initio methods used to make the predictions are theoretically sound, i.e. they are reliable in the general consideration of non-dynamic and dynamic electron correlation effects [7–10], host embedding effects [11], scalar and spin–orbit coupling relativistic effects [12,13], as well as in the specific application to  $f$  elements [14,15], and they lead not only to good transition energies [3,4], but also to good absorption and emission band shapes [2,5], which means that the

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computed vibrational frequencies and absolute values of the bond length shifts are approximately correct. However, a definite proof of the predictions on the sign of the bond length shifts can only be provided by experiments, e.g. by excited-state EXAFS measurements. It is very likely that experiments of this kind will be done in liquid solution. The uncertainties in these kinds of experiment are expected to be smaller for larger absolute values of the bond length shifts. Accordingly, we address in this paper the following questions: Do the signs of the  $f \rightarrow d$  bond length shifts depend on the ligand and on the solvent? What ligands and solvents give more negative  $f \rightarrow d(t_{2g})$  bond length shifts?

In order to provide answers to these questions, we present the results of ab initio embedded cluster calculations on the  $4f^{1-2}A_{2u}$ ,  $5d(t_{2g})^{1-2}T_{2g}$ , and  $5d(e_g)^{1-2}E_g$  states of the clusters  $(\text{CeF}_6)^{3-}$ ,  $(\text{CeCl}_6)^{3-}$ , and  $(\text{CeBr}_6)^{3-}$  embedded in cubic elpasolite hosts ( $\text{K}_2\text{NaGaF}_6$ ,  $\text{Cs}_2\text{NaYCl}_6$ , and  $\text{Cs}_2\text{NaYBr}_6$ , respectively), and in liquid acetonitrile,  $\text{CH}_3\text{CN}$ , as well as in vacuo. Furthermore, we present a quantitative analysis of the values of the  $f \rightarrow d$  bond length shifts in terms of the vibrational frequencies and the variations of the transition energies with the bond distance. By means of this analysis, which serves to clarify the reasons behind the different quantitative behavior of the bond length shifts in fluorides and chlorides, we show that the model of Judd and Morrison [16,17], proposed by Bettinelli and Moncorgé [18] to account for the reduction of the  $4f \rightarrow 5d$  transition energy experienced by lanthanide ions in crystals, and used by Dorenbos [19–22] in order to rationalize and predict  $4f \rightarrow 5d$  transitions in a large number of hosts, is insufficient because important repulsive contributions are missing. These missing terms are essential to understanding these transitions in the fluoride compounds.

## 2. Results and discussion

Firstly, we performed CASSCF calculations [7] with the CG-AIMP relativistic embedded cluster Hamiltonian [11,12] on the above-mentioned clusters embedded in AIMP representations of the elpasolite lattices produced in Refs. [23,24]. The active orbital space was made of the MOs with main character Ce  $4f$  and  $5d$ . All the relevant interactions for this problem except dynamic correlation are included at this stage, in which optimized molecular orbitals are produced. These MOs were used in a second step in CASPT2 calculations [8,9], where dynamic correlation from the 48 electrons in MOs of main character  $2s$  and  $2p$  of F,  $3s$  and  $3p$  of Cl, or  $4s$  and  $4p$  of Br, and from the 9 electrons in MOs of main character Ce  $5s$ ,  $5p$ , and  $4f$  or  $5d$  are included by means of multireference perturbation theory techniques. A [Kr] frozen-core Cowan-Griffin relativistic ab initio model

potential (CG-AIMP) was used for Ce, together with a  $(14s10p10d8f3g)/[6s5p6d4f1g]$  Gaussian basis set. A [He] frozen-core CG-AIMP was used for F with a  $(5s6p1d)/[3s4p1d]$  Gaussian basis set, a [Ne] frozen-core CG-AIMP was used for Cl with a  $(7s7p1d)/[3s4p1d]$  basis set, and a [Ar,3d] frozen-core CG-AIMP was used for Br with a  $(9s8p4d)/[3s4p2d]$  basis set. For the clusters in liquid  $\text{CH}_3\text{CN}$  solution we used the reaction field method with the Kirkwood model for a polarizable continuum of a given dielectric constant (38.8 for liquid acetonitrile at room temperature), in which a cluster is located in a spherical cavity within the polarizable medium, which is in turn polarized and creates a reaction field that acts back on the cluster. The problem is solved self-consistently. Using a conventional approach, the sizes of the cavities were optimized and ad hoc Pauli repulsion terms were added which prevent the cluster wave functions from collapsing onto the polarizable continuum [25,26]. All the calculations were performed with the program MOLCAS [27]. The results of our best calculations, CASPT2, are summarized in Tables 1 and 2 and in Fig. 1. The figure includes the bond length shifts resulting from the CASSCF calculations without dynamic correlation.

We observe that the bond length pattern

$$R_e[5d(t_{2g})^1] < R_e[4f^1] < R_e[5d(e_g)^1]$$

is the same for all ligands and solvents, with  $R_e[4f^1] \approx R_e[5d(e_g)^1]$  in the bromine compound (see below). Consistently with the analysis of interactions responsible for the bond length shifts [6], ligands giving more covalent interactions and with more electron donor character led to more negative values of  $\Delta R_e(f \rightarrow d(t_{2g})) = R_e[5d(t_{2g})^1] - R_e[4f^1]$ . With respect to solvent effects,

Table 1  
Computed bond lengths (Å) and breathing mode vibrational frequencies ( $\text{cm}^{-1}$ )

	In elpasolite		In acetonitrile		In vacuo	
	$R_e$	$\omega_{a1g}$	$R_e$	$\omega_{a1g}$	$R_e$	$\omega_{a1g}$
$(\text{CeF}_6)^{3-}$						
$4f^{1-2}A_{2u}$	2.163	678	2.308	475	2.379	348
$5d(t_{2g})^{1-2}T_{2g}$	2.154	681	2.285	487	2.344	371
$5d(e_g)^{1-2}E_g$	2.196	668				
$(\text{CeCl}_6)^{3-}$						
$4f^{1-2}A_{2u}$	2.687	307	2.816	236	2.863	206
$5d(t_{2g})^{1-2}T_{2g}$	2.645	308	2.757	242	2.787	213
$5d(e_g)^{1-2}E_g$	2.705	301	2.836	230		
$(\text{CeBr}_6)^{3-}$						
$4f^{1-2}A_{2u}$	2.792	198	2.924	153	2.970	135
$5d(t_{2g})^{1-2}T_{2g}$	2.746	201	2.859	159	2.893	144
$5d(e_g)^{1-2}E_g$	2.799	191	2.927	144	2.970	128

it can be seen in Fig. 1 that all solvents tend to diminish the size of the  $f \rightarrow d(t_{2g})$  bond length shift experienced by the isolated clusters. Moving from in vacuo to acetonitrile liquid solution to elpasolite solid solution means increasing the state of polarization of the medium surrounding the  $(\text{CeL}_6)^{3-}$  clusters (although solid elpasolites have much smaller dielectric constants than acetonitrile, they are a more polarized medium), so that the results indicate that the more polarized the solvent is, the more it diminishes the  $f \rightarrow d(t_{2g})$  bond length shift. This makes sense because a polarized medium stabilizes the halide anions, diminishing their ability for covalent bonding and electron donation, e.g. the interaction between a  $\text{Cl}^-$  and a  $\text{Na}^+$  is more covalent and with a larger charge transfer from the first to the

second in the diatomic molecule in the gas phase than in rock salt. We must expect the  $(\text{CeL}_6)^{3-}$  clusters to have bond length shifts within the limits shown in Fig. 1 in all liquid solvents that do not chemically interact with the halide ligands, because they would be polarized less than the solid elpasolites. This means they should be observable in excited-state EXAFS experiments in liquid solution.

The breathing mode vibrational frequencies follow the bond lengths: shorter bond lengths go together with larger force constants. We note that the vibrational frequencies of the three states are very similar for each ligand/solvent pair, as shown in Table 1.

As a means to estimate the precision of the predicted bond length shifts, as well as the vibrational frequencies, we calculated the  $4f \rightarrow 5d(t_{2g})$  and  $4f \rightarrow 5d(e_g)$  absorption band profiles of the chloride and bromide compounds in acetonitrile using wave packet propagation [28,29] as in previous cases [2,5]. We used an arbitrary value for the broadening factor of  $150 \text{ cm}^{-1}$  in order to simulate the effect of room temperature. We calculated the oscillator strengths of both compounds in order to be able to compare their intensities; their ratio is  $f((\text{CeBr}_6)^{3-})/f((\text{CeCl}_6)^{3-}) = 0.99$ . We show the results in Fig. 2. The  $4f \rightarrow 5d(t_{2g})$  profile compares very well with the room temperature experiment of Ryan and Jørgensen (see Fig. 4 of Ref. [30]), for which the wavelengths and relative intensities of the peaks are given by arrows. This indicates that the absolute value of the computed  $4f \rightarrow 5d(t_{2g})$  bond length shifts of the chloride and bromide compounds are reliable. We predict the  $4f \rightarrow 5d(e_g)$  absorption bands to be narrow; measurements of this absorption in liquid solution have not been reported to the best of our knowledge.

The transition energies shown in Table 2 follow the expected qualitative trends. Let us start with the energy

Table 2  
Computed minimum-to-minimum transition energies ( $\text{cm}^{-1}$ )

	In elpasolite	In acetonitrile	In vacuo
$(\text{CeF}_6)^{3-}$			
$4f \rightarrow 5d(t_{2g})$	27,100	30,700	31,300
$4f \rightarrow 5d(e_g)$	64,500		
$4f \rightarrow \langle 5d \rangle$	42,060		
$5d(t_{2g}) \rightarrow 5d(e_g)$	37,400		
$(\text{CeCl}_6)^{3-}$			
$4f \rightarrow 5d(t_{2g})$	24,300	27,700	28,200
$4f \rightarrow 5d(e_g)$	47,200	45,300	
$4f \rightarrow \langle 5d \rangle$	33,460	34,740	
$5d(t_{2g}) \rightarrow 5d(e_g)$	22,900	17,600	
$(\text{CeBr}_6)^{3-}$			
$4f \rightarrow 5d(t_{2g})$	22,200	25,700	26,700
$4f \rightarrow 5d(e_g)$	44,100	41,400	41,600
$4f \rightarrow \langle 5d \rangle$	30,960	31,980	32,660
$5d(t_{2g}) \rightarrow 5d(e_g)$	21,900	15,700	14,900

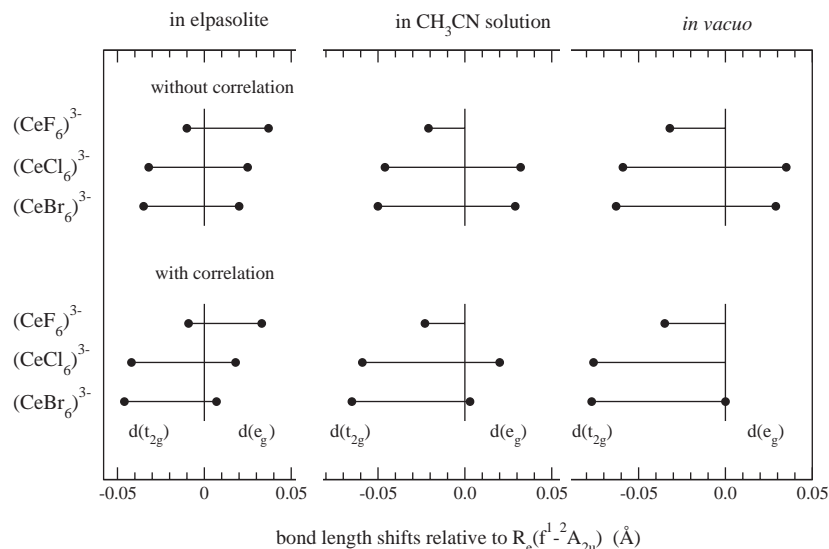


Fig. 1. Computed  $4f \rightarrow 5d(t_{2g})$  and  $4f \rightarrow 5d(e_g)$  bond length shifts. The results with correlation correspond to our best calculation, CASPT2.

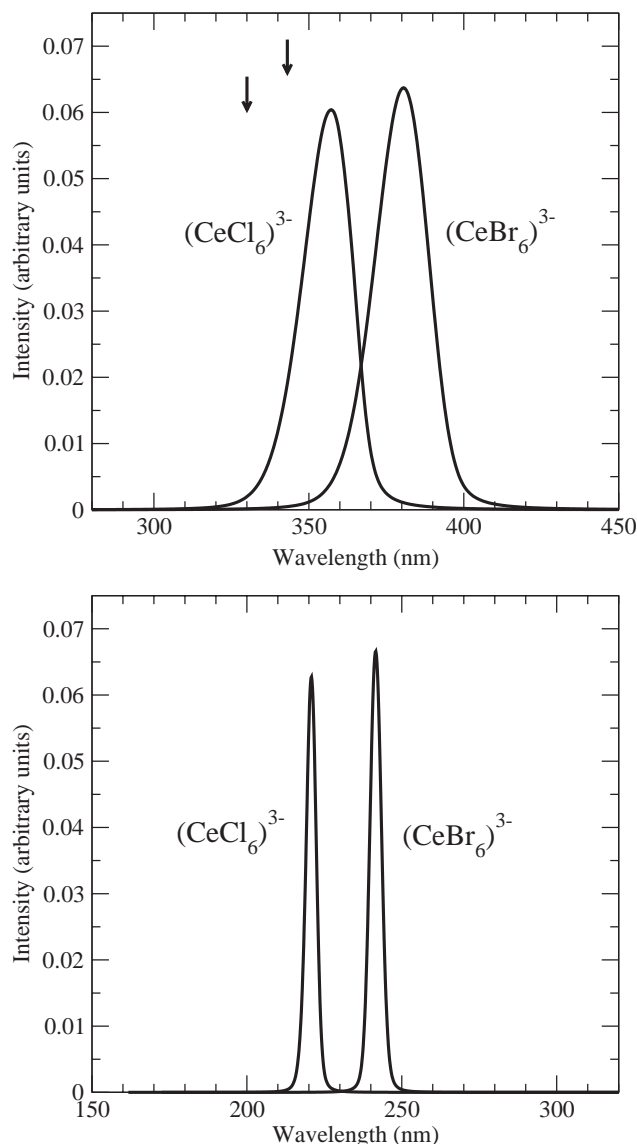


Fig. 2. Simulated  $4f \rightarrow 5d(t_{2g})$  (upper graph) and  $4f \rightarrow 5d(e_g)$  (lower graph) room temperature absorption band shapes of  $(\text{CeCl}_6)^{3-}$  and  $(\text{CeBr}_6)^{3-}$  in acetonitrile solution. Arrows in the upper graph indicate the experimental peaks. The points of the arrows indicate the intensities taken from Fig. 4 of Ref. [30].

differences between the two  $5d$  ligand field split states,  $5d(t_{2g}) \rightarrow 5d(e_g)$ , which correspond to the crystal field theory parameter  $10Dq$  and are a measure of the effective ligand fields. They show that the effective ligand field decreases from F to Br ligands and from more polarized to less polarized solvents. Using these data, one can define the energy of the center of gravity or baricenter state of the  $5d^1$  configuration as the weighted average of the  $5d(t_{2g})^1 - {}^2T_{2g}$  and  $5d(e_g)^1 - {}^2E_g$  states, so that the transitions  $4f \rightarrow 5d(t_{2g})$  and  $4f \rightarrow 5d(e_g)$  can be regarded as the transition to the baricenter,  $4f \rightarrow \langle 5d \rangle$ , minus  $\frac{2}{5}$  and plus  $\frac{3}{5}$  of the  $5d(t_{2g}) \rightarrow 5d(e_g)$  one respectively. At first sight, the

$4f \rightarrow \langle 5d \rangle$  transition energy follows qualitatively the model of Judd–Morrison, according to which it equals the  $\text{Ce}^{3+}$  free-ion transition energy minus a contribution which depends on the ligand polarizability,  $\alpha_L$  and the Ce–Ligand distance:

$$\Delta E(4f \rightarrow \langle 5d \rangle)_{\text{CeL}_6^{3-}} - \Delta E(4f \rightarrow \langle 5d \rangle)_{\text{Ce}^{3+}} \approx -(\langle r^2 \rangle_{5d} - \langle r^2 \rangle_{4f}) \sum_L \frac{\alpha_L e^2}{R_{\text{Ce-L}}^6}. \quad (1)$$

In effect, from  $\text{F}^-$  to  $\text{Br}^-$  ligands the transition is diminished, as the ligand polarizability increases; since the bond length gives the opposite trend (it is larger in bromide compounds), it appears that it is the effect of the ligand polarizability that controls the tendency. Changing solvent for a given ligand should have little effect on the ligand polarizability and the effect must be controlled by the bond length: longer bond lengths from elpasolite to acetonitrile to gas phase go together with larger  $4f \rightarrow \langle 5d \rangle$  transition energies. However, as shown below, this description seems to be oversimplified.

Before discussing the limits of application of the Judd–Morrison model for the  $f \rightarrow d$  transitions of f-element ion complexes, let us comment on the fact that the effective ligand field diminishes significantly from  $\text{F}^-$  to  $\text{Cl}^-$  (or  $\text{Br}^-$ ) ligands according to the  $\Delta E(t_{2g} \rightarrow e_g)$  transition energies, whereas  $\Delta R_e(t_{2g} \rightarrow e_g)$  experiences a significant increase, an apparent contradiction in the effects of the ligand field. However, this can be understood as a consequence of the bond force constant largely diminishing from  $\text{F}^-$  to  $\text{Cl}^-$ . Let us discuss this in some detail: The energy of an electronic state  $i$  at a given nuclear configuration of the breathing mode near its minimum can be expressed as

$$E_i(R) = E_{0,i} + \frac{1}{2}k_i(R - R_{0,i})^2 + \dots \quad (2)$$

and the corresponding force acting on the ligands as

$$F_i = -E'_i = -\frac{dE_i}{dR} = -k_i(R - R_{0,i}) + \dots \quad (3)$$

Let us call the difference in the atomic forces induced by the  $i \rightarrow f$  transition ( $-\frac{d}{dR}(E_f - E_i)$ ), the Frank–Condon force  $F_{\text{FC}}(i \rightarrow f)$ , because it is the force acting on the atoms in the  $f$  state at the equilibrium of the  $i$  state. If the bond force constants of the initial and final states involved in an electronic transition are similar (which is the case here),  $k_i \approx k_f \approx k$ , then  $F_{\text{FC}}(i \rightarrow f) = -\Delta E'(i \rightarrow f) = k(R_{0,f} - R_{0,i}) + \dots$ , and the  $i \rightarrow f$  bond length shift is:

$$\begin{aligned} \Delta R_e(i \rightarrow f) &= R_{0,f} - R_{0,i} \approx \frac{F_{\text{FC}}(i \rightarrow f)}{k} \\ &= \frac{-\Delta E'(i \rightarrow f)}{k}. \end{aligned} \quad (4)$$

This allows for an analysis of the bond length shifts if the force constants and the slopes of the transition

energies are known. The results of the present ab initio calculations are shown in Table 3. The validity of this analysis in the case of the  $t_{2g} \rightarrow e_g$  bond length shift is supported by comparing the third and fourth rows. The values of  $\Delta E'(t_{2g} \rightarrow e_g)$  (second row) simply confirm the qualitative prediction of crystal field theory that the  $R$  derivative of the ligand field is negative (which is the ultimate reason for the bond length increase) and its absolute value increases with the ligand field itself [in CFT:  $d(10Dq)/dR = -5(10Dq)/R$ ], although the quantitative variation is different (it follows  $R^{-3.6}$ ,  $R^{-3.9}$ , and  $R^{-3.5}$  laws for the fluoride, chloride, and bromide compounds respectively, according to our calculations). What is interesting to see is that the significant increase of  $\Delta R_e(t_{2g} \rightarrow e_g)$  from the fluoride to the chloride compounds by a factor of approximately 1.45, is the result of two opposite contributions, namely, a lowering due to the lower absolute value of the transition energy slope (which is the consequence of a lower field) and a large, dominant increment due to the reduction in the force constant (with a factor of 2.63):

$$\frac{\Delta R_e(t_{2g} \rightarrow e_g)_{\text{Cl}}}{\Delta R_e(t_{2g} \rightarrow e_g)_{\text{F}}} \approx \frac{\Delta E'(t_{2g} \rightarrow e_g)_{\text{Cl}}}{\Delta E'(t_{2g} \rightarrow e_g)_{\text{F}}} \times \frac{k_{\text{F}}}{k_{\text{Cl}}} = 0.56 \times 2.63 \quad (5)$$

The same quantitative analysis can be fruitfully applied to the  $f \rightarrow d$  bond length shifts using the slope of the transition energy to the  $d$  baricenter (fifth row of Table 3) and the fact that the individual transitions can be described as the transition to the baricenter minus/plus fractions of the  $5d$  effective ligand field splitting. Firstly, the chloride and bromide compounds exhibit positive slopes of the  $f \rightarrow \langle d \rangle$  transitions, which mean significant contributions to inwards distortions upon  $f \rightarrow d$

excitation in both compounds. Interestingly, although this disagrees with the usual assumption that this excitation provides an outwards distortion, it is in qualitative agreement with the Judd–Morrison model presently accepted to describe the energies of the  $f \rightarrow d$  transitions, according to which these energies should be smaller at shorter distances and, so, the  $f \rightarrow d$  transitions should cause an inwards distortion. The total distortions produced by the individual transitions are obtained after adding the effective ligand field effects, which are larger in size due to the larger transition energy slopes. They significantly enhance the inwards distortion of the  $f \rightarrow d(t_{2g})$  excitation. Simultaneously, they reverse the sign of the distortion produced by the  $f \rightarrow d(e_g)$  excitation; in the bromide compound this effect compensates the inwards tendency of the  $f \rightarrow \langle d \rangle$  almost perfectly, because the slope of the  $f \rightarrow \langle d \rangle$  transition energy and  $\frac{3}{5}$  of the slope of the  $d(t_{2g}) \rightarrow d(e_g)$  transition energy are almost equal in magnitude and of opposite sign. Thus, the bond length does not change significantly upon  $f \rightarrow d(e_g)$  excitation.

However, the fluoride shows a negative slope of  $\Delta E(f \rightarrow \langle d \rangle)$ . This pulls the bonds slightly, so that their overall shrinking is entirely due to the ligand field effects. This result indicates that the Judd–Morrison model is insufficient to account for the  $f \rightarrow d$  transitions in  $f$ -element ion complexes because it only considers attractive interactions that predict the  $R$  derivative of the  $f \rightarrow d$  transition energies to be positive. Repulsive interactions must also be present because, in a molecular orbital theory description, these are basically non-bonding to antibonding MO transitions. As we have just seen, the repulsive interactions leading to a negative slope of  $\Delta E(f \rightarrow \langle d \rangle)$  are dominant in  $(\text{CeF}_6)^{3-}$ . In this fluoride, the effects due to the ligand field splitting of the  $d$  orbitals are the key factor.

Table 3

Computed bond stretching force constants ( $\text{cm}^{-1}/\text{\AA}^2$ ), Frank-Condon forces (negative bond length derivatives of the transition energies) ( $\text{cm}^{-1}/\text{\AA}$ ), and analysis of the  $4f \rightarrow 5d(t_{2g})$  and  $5d(t_{2g}) \rightarrow 5d(e_g)$  bond length shifts ( $\text{\AA}$ ), for the clusters  $(\text{CeF}_6)^{3-}$ ,  $(\text{CeCl}_6)^{3-}$ , and  $(\text{CeBr}_6)^{3-}$  in elpasolite hosts

	Units	$(\text{CeF}_6)^{3-}$	$(\text{CeCl}_6)^{3-}$	$(\text{CeBr}_6)^{3-}$
$k$	$\text{cm}^{-1}/\text{\AA}^2$	$15.4 \times 10^5$	$5.86 \times 10^5$	$5.48 \times 10^5$
$\Delta E'(t_{2g} \rightarrow e_g)$	$\text{cm}^{-1}/\text{\AA}$	−63700	−35500	−28700
$F_{\text{FC}}(t_{2g} \rightarrow e_g)/k$	$\text{\AA}$	0.041	0.061	0.052
$\Delta R_e(t_{2g} \rightarrow e_g)$	$\text{\AA}$	0.042	0.060	0.053
$\Delta E'(f \rightarrow \langle d \rangle)$	$\text{cm}^{-1}/\text{\AA}$	−9980	11400	15010
$F_{\text{FC}}(f \rightarrow \langle d \rangle)/k$	$\text{\AA}$	0.006	−0.019	−0.027
$\frac{2}{5} \Delta E'(t_{2g} \rightarrow e_g)/k$	$\text{\AA}$	−0.016	−0.024	−0.021
$F_{\text{FC}}(f \rightarrow t_{2g})/k$	$\text{\AA}$	−0.010	−0.043	−0.048
$\Delta R_e(f \rightarrow t_{2g})$	$\text{\AA}$	−0.009	−0.042	−0.046
$-\frac{3}{5} \Delta E'(t_{2g} \rightarrow e_g)/k$	$\text{\AA}$	0.025	0.037	0.031
$F_{\text{FC}}(f \rightarrow e_g)/k$	$\text{\AA}$	0.031	0.018	0.004
$\Delta R_e(f \rightarrow e_g)$	$\text{\AA}$	0.033	0.018	0.007

### 3. Conclusions

Previous predictions of bond length shortening experienced by  $f$ -element hexachlorides in ionic solid hosts upon  $4f \rightarrow 5d(t_{2g})$  and  $5f \rightarrow 6d(t_{2g})$  excitations are confirmed here and extended to hexafluorides and hexabromides of  $\text{Ce}^{3+}$ . This behavior is also predicted to be present in liquid solutions. Chloride and bromide compounds in liquid acetonitrile are good candidates for excited-state EXAFS measurements to determine the sign of the bond length changes. Also, the change of bond length upon electronic excitation is related to the Frank–Condon force (the force acting on the atoms in the final state at the equilibrium nuclear configuration of the initial state) and the force constant. This expression is used to explain the dependence of the bond length shifts  $\Delta R_e(t_{2g} \rightarrow e_g)$  on the effective ligand field, which might seem anomalous at first sight. Finally, the present



ab initio calculations give negative values for the slope of the excitation energy  $\Delta E(f \rightarrow \langle d \rangle)$  of  $(\text{CeF}_6)^{3-}$  with respect to the Ce–F bond distance; this result contradicts the Judd–Morrison model used for the interpretation of the  $f \rightarrow d$  transitions, which predicts positive values in all cases.

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