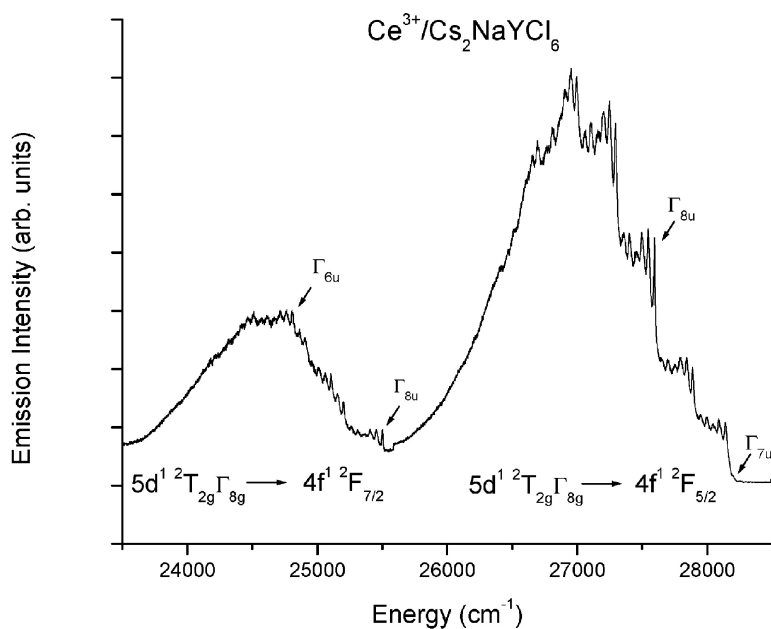


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J. Am. Chem. Soc., **2003**, 125 (43), 13225-13233 • DOI: 10.1021/ja036659x • Publication Date (Web): 04 October 2003

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Absorption and Emission Spectra of Ce³⁺ in Elpasolite Lattices

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Abstract: The experimental determination of the electronic energy levels for Ce³⁺ in some chloroelpasolite hosts for both the ground 4f¹ and the excited 5d¹ configurations is described. High-resolution f–f absorption and f–²T_{2g} d absorption and emission spectra have been recorded at low temperatures for Ce³⁺ diluted into various hexachloroelpasolite lattices. A fluorescence spectrum at ~50 000 cm⁻¹ is tentatively assigned to the emission from the highest 5d crystal field level, ²E_g, of a Ce³⁺ impurity in Cs₂NaErCl₆, enabling the values of all the energy levels of both the 4f¹ and 5d¹ configurations to be given for Ce³⁺ in elpasolite hosts. Vibronic structure superimposed on the electronic transitions is analyzed in terms of a simple configurational coordinate model involving the ground and excited configurations. It is found that the difference in the Ce–Cl bond length between the 4f¹ and 5d¹ configurations is ~0.04 Å. Ab initio model potential calculations on the (CeCl₆)³⁻ cluster embedded in a reliable representation of the Cs₂NaYCl₆ host support these conclusions.

Introduction

At the beginning of the 4f and the 5f transition series, the f and d electronic configurations of the di-, tri-, and tetravalent free ions are very close in energy.^{1,2} This is also true for these ions in compounds. For example, the lowest energy configuration for the Ce²⁺ free ion is [Xe core]4f² with the beginning of the opposite parity 4f5d configuration at 3277 cm⁻¹. However, in a CaF₂ host, the ground configuration is [Xe core]-4f5d.³ The Ce³⁺ free ion has a 4f¹ ground configuration with the lowest 5d state at 47 937 cm⁻¹.¹ When this ion is placed in a crystal, the lowest 4f to 5d electric dipole allowed transition has been reported to be in the range of 20 000 to 40 000 cm⁻¹ depending on the particular compound or matrix investigated.⁴ Similarly, for the actinide or 5f series, the lowest 5f–6d transition for the Pa⁴⁺ ion diluted in Cs₂ZrCl₆ is at 20 000 cm⁻¹, but the free ion separation between ground 5f level and the first

6d level is ~50 000 cm⁻¹.⁵ In the few structurally characterized Th³⁺ organometallic compounds, the 6d¹ configuration has been found to be the ground configuration,^{6,7} but the ground term is from the 5f configuration and the first 6d level is 10 000 cm⁻¹ higher in the Th³⁺ free ion. The U³⁺ ion in the LaCl₃ host has the first 5f³ to 5f²6d¹ transition at approximately 22 000 cm⁻¹, although in the U³⁺/RbY₂Cl₇ system this transition is found at ~14 000 cm⁻¹.⁸ Thus, as the degree of ionization increases and/or the atomic number is increased (for both the lanthanide and the actinide series), the fⁿ configuration becomes increasingly stabilized so that the interconfigurational transitions are not observed in the visible or near-ultraviolet region. Only at the beginning of both the lanthanide and actinide series is it possible to observe these interconfigurational transitions in this energy range.

For the lanthanide series, the Ce³⁺ ion has been extensively studied and measured levels have been reported for both the ground 4f¹ configuration and the excited 5d¹ configuration. Figure 1 shows schematically the energy levels and nomenclature used for the 4f¹ and 5d¹ configurations of the Ce³⁺ ion diluted in choroelpasolite hosts. The 6 K 4f–5d absorption and

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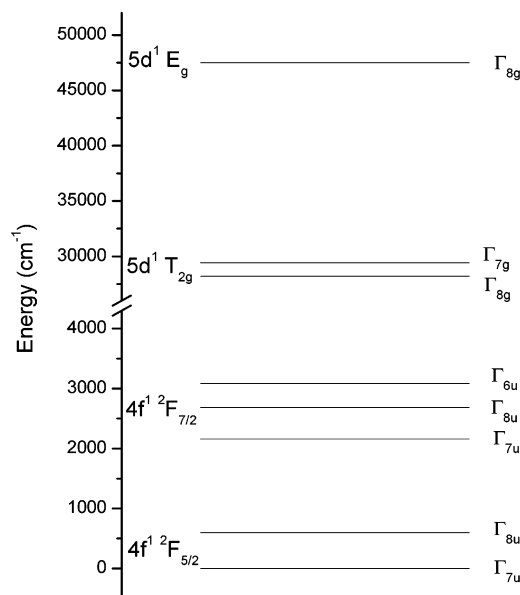


Figure 1. Schematic energy level diagram of the $4f^1$ and $5d^1$ configurations of the Ce^{3+} ion in a chloroelpasolite crystal field. Note the change in the energy scale between the $4f^1$ and the $5d^1$ configurations.

magnetic circular dichroism (MCD) spectra of Ce^{3+} diluted in Cs_2NaYCl_6 were reported by Schwartz and Schatz.⁹ They located the $5d^1 T_{2g} \Gamma_8$ and Γ_7 levels at $28\,196\text{ cm}^{-1}$ and $29\,435\text{ cm}^{-1}$, respectively. No further electronic absorption transitions were detected up to $50\,000\text{ cm}^{-1}$. The $5d^1 E_g \Gamma_8$ level was thus assumed to be $>20\,000\text{ cm}^{-1}$ above the $2T_{2g}$ baricenter. The EPR spectrum of the Ce^{3+} ion in Cs_2NaYCl_6 has also been measured.¹⁰ The $5d-4f$ luminescence from the $2T_{2g}$ state was recently reported under low resolution at 80 K, with about a 30 ns lifetime.¹¹ The decay curves for X-ray- and vacuum ultraviolet-excited emission of Ce^{3+}/Cs_2LiYCl_6 and $Ce^{3+}/Cs_2LiLaCl_6$ have recently been reported.^{12,13} Ionova et al. have cited the lowest $\pi \rightarrow f$ charge-transfer band in $CeCl_6^{3-}$ near $60\,000\text{ cm}^{-1}$.¹⁴

van't Spijker et al.¹⁵ reported the excitation spectra of the 425 nm ($23\,530\text{ cm}^{-1}$) emission of Ce^{3+} in $Cs_2NaLaCl_6$, $Cs_2NaCeCl_6$, and $Cs_2NaLuCl_6$. In each case, bands were observed near 210 nm and attributed to $f-2E_g d$ transitions of Ce^{3+} . The wavelengths of these bands have been listed by Dorenbos,¹⁶ with the addition of 210, 217 nm ($47\,620, 46\,083\text{ cm}^{-1}$) for Ce^{3+}/Cs_2NaYCl_6 . For O_h symmetry, only one band is expected in this energy range, but multiple sites are often observed for lanthanide impurities in these hosts. Hence it is well-substantiated that the $2E_g$ state is near $47\,000\text{ cm}^{-1}$ in these cubic elpasolite hosts. This state also has been observed at $42\,200\text{ cm}^{-1}$ in the 300 K photoacoustic spectrum of Ce^{3+}/BaF_2 .¹⁷

Rodnyi et al.¹³ observed bands in the 300 K excitation spectrum of the 3.3 eV luminescence of Ce^{3+} in $Cs_2LiLaCl_6$ at

$35\,730, 37\,908, 41\,134, \text{ and } 45\,247\text{ cm}^{-1}$, which were assigned to $f-d$ transitions of Ce^{3+} . The 19 eV-excited emission spectrum of $Cs_2LiLaCl_6$ doped with 1% Ce^{3+} gave a broad band at $26\,616\text{ cm}^{-1}$, assigned to $d-f$ emission of Ce^{3+} , in addition to a broader feature ($33\,069\text{ cm}^{-1}$) assigned to core-valence luminescence. No emission was evident from the $2E_g$ state of Ce^{3+} .

In a more recent study of Ce^{3+} -doped Cs_2LiYX_6 ,¹⁸ even the neat Cs_2LiYCl_6 showed extensive bands between $48\,000-100\,000\text{ cm}^{-1}$ in the excitation spectra of the "host" emission at $29\,036\text{ cm}^{-1}$. The 130 K excitation spectrum of Ce^{3+}/Cs_2LiYCl_6 (monitoring the Ce^{3+} emission at $25\,003\text{ cm}^{-1}$) showed additional bands at roughly $27\,000-32\,000, 36\,300, 42\,700, \text{ and } 50\,000\text{ cm}^{-1}$. The $36\,300$ and $42\,750\text{ cm}^{-1}$ bands were assigned to Ce^{3+} transitions: the lower energy band being due to a lower symmetry site, and the $50\,000\text{ cm}^{-1}$ band to the $2E_g$ state. No emission was observed from the $2E_g$ level in Ce^{3+} -doped Cs_2LiYX_6 under X-ray excitation, but emission from the $2T_{2g}$ level was observed.

In this paper, we report the experimental determination of the electronic energy levels for Ce^{3+} in some chloroelpasolite hosts for both the ground $4f^1$ and the excited $5d^1$ configurations. A preliminary account of the emission spectra from the lowest $5d$ level of Ce^{3+} in Cs_2NaYCl_6 to the $4f^1$ energy levels has been given.¹⁹ We have recorded an emission spectrum of $Cs_2NaErCl_6$ at $\sim 50\,000\text{ cm}^{-1}$, which we tentatively assign to the emission from the highest $5d$ crystal field level of a Ce^{3+} impurity. Although the magnitude of the crystal field at the Ce^{3+} site in $Cs_2NaErCl_6$ is not quite the same as that for Cs_2NaYCl_6 , the differences should be relatively small since the ionic radii of Er^{3+} and Y^{3+} are similar. If the assumption is made that the differences in the crystal field strength are negligible, accurate data are available for both the $4f^1$ and $5d^1$ configurations in the elpasolite host. These data are analyzed, and the parameters evaluated using the crystal field model.

We also report the results of supportive ab initio embedded cluster calculations^{20,21} on $(CeCl_6)^{3-}/Cs_2NaYCl_6$.

Experimental Section

$Cs_2NaCeCl_6$ and other (Ce-doped) hexachloroelpasolites were prepared according to Morss method E.²² The powders were passed through a Bridgman furnace at ca. $850\text{ }^\circ\text{C}$ in vacuo in quartz tubes to give polycrystalline materials. The purity of the lanthanide oxides employed was 99.999% for Pr_2O_3 , 99.9% for Tm_2O_3 , 99.999% for Er_2O_3 (all from Strem Chemicals), and 99.999% for Y_2O_3 (Berkshire Ores). $CeCl_3$ (99.9%, Strem) was used to prepare neat $Cs_2NaCeCl_6$ and Ce-doped Cs_2LiYCl_6 . ICP-AES analyses showed that the Y_2O_3 contained (relative to Y) 58 ppm Ce, 120 ppm Pr, and 17 ppm Nd. Similar analyses, by direct calibration and by standard addition, were attempted for the Er_2O_3 material but reliable data could not be obtained.

Infrared and absorption spectra were recorded using a Biorad FTS-60A spectrometer, equipped with DTGS and photomultiplier detectors, and using an Oxford Instruments closed-cycle cryostat with base temperature 10 K. Ultraviolet and emission spectra were also recorded using a D_2 lamp or 355 nm radiation from a Nd:YAG laser, together with a 0.5 m Acton monochromator equipped with a charge-coupled device. Raman spectra were recorded as described previously.²³ Some

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Table 1. f and d Electron Energy Levels (in cm⁻¹) of Ce³⁺ in Elpasolite Lattices

configuration (^{2S+1} L) _J	irrep	electronic	electronic	electronic	electronic	fluorescence	fluorescence	fluorescence
		Raman, Cs ₂ NaCeCl ₆ 20 K	absorption, Cs ₂ NaCeCl ₆ 90 K	absorption, Ce ³⁺ /Cs ₂ NaYCl ₆ 10 K	absorption, Ce ³⁺ /Cs ₂ NaTmCl ₆ 90 K	Ce ³⁺ /Cs ₂ NaErCl ₆ 10 K	Ce ³⁺ /Cs ₂ NaYCl ₆ 10 K	Ce ³⁺ /Cs ₂ LiYCl ₆ 10 K
4f ¹ ² F _{5/2}	Γ _{7u}	0	0	0	0	0	0	0
	Γ _{8u}	562, 580	563, 575			594	599	578
4f ¹ ² F _{7/2}	Γ _{7u}	2161	2159	2159	2157	2125		
	Γ _{8u}	2663	2659	2674	(2676)	2628	2689	2674
	Γ _{6u}	3050	3048				3086	3061
5d ¹ T _{2g}	Γ _{8g}			28 196			28 193	28 265
	Γ _{7g}			29 435				
5d ¹ E _g	Γ _{8g}					47 080		

experiments were also performed at Hong Kong University, where the anti-Stokes H₂-shifted harmonics of an Nd-YAG pulsed laser were used to excite polycrystalline Ce/Cs₂NaYCl₆ and Cs₂NaErCl₆ (assumed to contain traces of Ce³⁺) with the equipment described earlier.²⁴ The spectral resolution was between 2 and 4 cm⁻¹. Spectral calibration was performed using various standard lamps, and the wavelengths were corrected to vacuum.

Fluorescence spectra obtained at LBNL from the lowest 5d level to the 4f manifolds were obtained using a xenon lamp as described previously.²⁵ The sample was cooled to ~10 K using an Oxford Instruments model 1204 cryostat. The entrance and exit slits of the Spex 1403 double monochromator were set at 200 μm for a resolution on the order of 1 cm⁻¹. The spectra were calibrated with a mercury lamp and corrected to vacuum.

Review of Parametric Theory. The Hamiltonian for the energy levels of an f electron in an octahedral crystal field may be written as²⁶

$$H = H_{SO} + H_{CF}$$

$$H_{SO} = \zeta_{4f}(r) \mathbf{l} \cdot \mathbf{s}$$

$$H_{CF} = B_0^4 [C_0^4 + (\zeta_{14}^5)^{1/2} (C_{-4}^4 + C_4^4)] + B_0^6 [C_0^6 - (\zeta_{12}^7)^{1/2} (C_{-4}^6 + C_4^6)] \quad (1)$$

The empirical parameters above include the crystal field parameters B_0^4 and B_0^6 (utilizing the Wybourne notation) and the spin-orbit coupling constant $\zeta_{4f}(r)$. The matrix elements for the angular momentum operators \mathbf{s} and \mathbf{l} and the tensor operators C_q^k depend only on the angular coordinates and are evaluated by standard techniques.^{26,27} For the 4f¹ configuration of Ce³⁺/Cs₂NaYCl₆, the spin-orbit interaction is larger than the crystal field interaction. The spin-orbit coupling interaction splits the f¹ free ion state into two J levels, $J = 5/2$ and $7/2$, and the octahedral crystal field splits the ground $J = 5/2$ term into a Γ_{7u} doublet and a Γ_{8u} quartet, using the double group notation for octahedral symmetry. Similarly, the $J = 7/2$ term splits into two doublets of Γ_{7u} and Γ_{6u} symmetry and one quartet of Γ_{8u} symmetry. Figure 1 shows the approximate energy level diagram and the nomenclature used.

The above Hamiltonian may also be utilized for the 5d configuration. In this case, the sixth order crystal field term B_0^6 is equal to zero and the spin-orbit coupling constant is $\zeta_{5d}(r)$. However, unlike for the 4f configuration, the 5d configuration experiences a crystal field interaction that is considerably larger than the 5d spin-orbit coupling. The octahedral (O_h) crystal field splits the 5d¹ configuration into two levels, a triply orbitally degenerate T_{2g} lower state and a doubly orbitally degenerate E_g upper state. When the spin-orbit interaction is included, the T_{2g} level splits into a quartet Γ_{8g} lower level and a higher-lying doubly degenerate Γ_{7g} state. The E_g upper state transforms into a quartet Γ_{8g} state as shown in Figure 1. The solutions of the above Hamiltonian for a 4f¹ electron configuration or of the corresponding Hamiltonian for a 5d¹ electron configuration are well-known and will not be repeated.²⁸

The emission and absorption transitions reported in this paper between the 4f¹ and 5d¹ configurations are allowed electric dipole

transitions that originate or terminate in crystal field states of either Γ_{7u}, Γ_{8u}, or Γ_{6u} symmetry for the 4f¹ configuration or Γ_{8g} or Γ_{7g} for the 5d¹ configuration. The electric dipole operator transforms as Γ_{4u}. Evaluating the direct products of the initial and final states with the electric dipole operator shows all purely electronic zero phonon transitions are allowed, with the exception of Γ_{7g}-Γ_{6u}. The f ↔ d transitions between crystal field states may couple with totally symmetric vibrational modes, whereas in addition the τ_{2g} mode is potentially Jahn-Teller active for transitions between Γ₇ and Γ₈ states.

f-f Absorption Spectra. The 4f¹ crystal field levels of Cs₂NaCeCl₆ have been deduced from earlier electronic Raman, absorption, and emission studies and are given in Table 1.^{23,29} A crystal field fit gave $\zeta_{4f} = 623$ cm⁻¹, $B_0^4 = 2119$ cm⁻¹ and $B_0^6 = 261$ cm⁻¹.³⁰ The f-f electronic absorption spectra of Ce³⁺/Cs₂NaYCl₆ and Cs₂NaCeCl₆ have been reported and are dominated by magnetic dipole transitions.³¹ Although the former is cubic at low temperatures, the latter undergoes a phase transition at 178 K.^{10,32-34} The infrared absorption spectra were reinvestigated in this study and the derived energy levels are listed in Table 1. The magnetic dipole transitions (²F_{5/2})Γ₇ → (²F_{7/2})Γ₇, Γ₈ are the most intense bands, with measured oscillator strengths 4.8×10^{-8} and 5.1×10^{-8} respectively in dilute Ce³⁺/Cs₂NaYCl₆. The fact that values measured in neat Cs₂NaCeCl₆ are smaller (6.3×10^{-9} and 1.7×10^{-8} , respectively) is attributed to saturation effects.

Vibrational Spectra. The normal vibrations of the Cs₂NaCeCl₆ crystal are described in the notation of Lentz, with the relationship to the CeCl₆³⁻ moiety mode vibrations being given in columns 1 and 2 of Table 2.³⁵ Assignments are included from the Raman and vibronic spectra. The energies of the stretching vibrations are somewhat higher in the Cs₂NaYCl₆ lattice, with ν₁, for example, being near 300 cm⁻¹. Also included in Table 2 are the results from normal coordinate calculations employing moiety mode and unit cell group models.^{36,37}

4f¹ ²F_{5/2}-5d¹ (²T_{2g}) Absorption Spectra. The 6 K ultraviolet electronic absorption spectrum of Ce³⁺/Cs₂NaYCl₆ has previously been reported by Schwarz and Schatz.⁹ It comprises electric dipole allowed transitions from the 4f¹ ²F_{5/2} Γ_{7u} ground state to the 5d¹ ²T_{2g} Γ_{8g} and

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Table 2. Vibrational Assignments for Cs₂NaCeCl₆

unit cell group mode and O _h point and group irrep.	moiety mode and O _h point group irrep.	20 K Raman spectrum (cm ⁻¹)	90 K f-f vibronic spectra (cm ⁻¹)	calcd ^b (cm ⁻¹)	calcd ^c (cm ⁻¹)
S ₁ Ce—Cl sym. str.	ν_1 (α_{1g})	279		279	279
S ₂ Ce—Cl str.	ν_2 (ϵ_g)	222		222	224
S ₃ rotatory lattice (τ_{1g})			(~20) ^a		21
S ₄ Cl—Ce—Cl bend	ν_5 (τ_{2g})	111		108	114
S ₅ Cs transl. (τ_{2g})		46			48
S ₆ Ce—Cl ant. str.	ν_3 (τ_{1u})		253(TO); 279(LO)	257	257
S ₇ Cl—Ce—Cl bend	ν_4 (τ_{1u})		98(TO); 119(LO)	106	112
S ₈ Na—Cl str. (τ_{1u})			(173) ^a		168
S ₉ Cs transl. (τ_{1u})			56(TO); 69(LO)		53
S ₁₀ Cl—Ce—Cl bend	ν_6 (τ_{2u})		74–84	77	76

^a From the spectra of Cs₂NaPrCl₆; TO/LO transverse/longitudinal optic modes; str., stretch; sym., symmetric; ant., antisymmetric; trans., translatory.
^b Using 5-parameter general valence force field for moiety modes.³⁶ ^c Using 9-parameter unit cell group model.³⁷

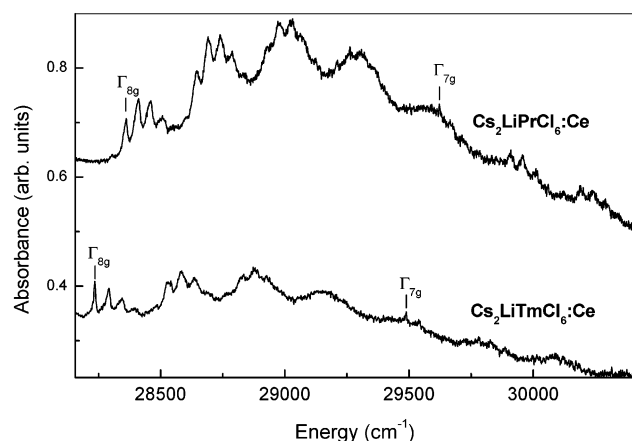


Figure 2. Absorption spectra (10 K) of trace Ce³⁺ impurity in Cs₂LiPrCl₆ and Cs₂LiTmCl₆ between 28 000 and 31 000 cm⁻¹. (The initial state is Γ_{7u} in all cases, and the terminal d-electronic states are labeled.)

Table 3. f-d Absorption Spectra of Ce³⁺ in Elpasolite Lattices

lattice	lattice parameter ^a (Å)	energy from ² F _{5/2} Γ_{7u} (cm ⁻¹)		energy difference (cm ⁻¹)
		² T _{2g} Γ_{8g}	² T _{2g} Γ_{7g}	
Cs ₂ NaYCl ₆	10.733	28 195 ± 2	29 435	1240
Cs ₂ LiPrCl ₆	10.651	28 363	29 625	1262
Cs ₂ LiTmCl ₆	10.439	28 236	29 489	1253
Cs ₂ LiYCl ₆	10.479	28 267		

^a From Meyer.⁵⁴

Γ_{7g} states. Prominent vibrational progressions in modes of 300 and 47 cm⁻¹ were built upon the zero phonon lines. We have reinvestigated the spectra at 10 K, and our spectrum is very similar to that of Schwarz and Schatz, with fine structure in addition to the two prominent progressions. A further progression in a lattice mode of ca. 14–16 cm⁻¹ was reported by Schwarz and Schatz, although the first member is not evident in the present study or in their published spectrum. However, we do observe a shoulder at 32 cm⁻¹ above the zero phonon line, in agreement with Schwarz and Schatz.

The 10 K absorption spectra of neat Cs₂LiPrCl₆ and Cs₂LiTmCl₆ in the ultraviolet show f-d absorption bands due to Ce³⁺ impurities (Figure 2). The zero phonon line transition energies are listed in columns 3 and 4 of Table 3. The weak feature to the low energy of $\Gamma_{7u} \rightarrow \Gamma_{8g}$ in Ce³⁺/Cs₂LiPrCl₆ is a hot band. The low energy part of the Ce³⁺/Cs₂LiTmCl₆ absorption spectrum overlaps the ³H₆–¹D₂ f-f transition of Cs₂LiTmCl₆. Samples of elpasolite hosts doped with Ce³⁺ concentra-

tions of the order of 1% exhibit total absorption in this region. The vibrational progression frequencies, averaged over all the first members, are listed for the two strongest progression modes in column 4 of Table 4.

²T_{2g} 5d¹–4f¹ ²F_{5/2}, ²F_{7/2} Emission Spectra. The Xe lamp-excited ~10 K emission spectrum of dilute Ce³⁺/Cs₂NaYCl₆ is shown in Figure 3. Transitions are observed to the ²F_{5/2}, ²F_{7/2} terminal crystal field levels of Ce³⁺, as marked in Figure 3, and the derived energies are listed in column 3 of Table 5. The lowest energy electronic origin is mostly self-absorbed, as is shown by the superposition of the absorption and 199.8 nm excited emission spectra from the 5d¹ level, both at 10 K (Figure 4). The mirror-image relationship of the broad absorption and emission spectra is not exact because, although the zero phonon transitions of the lowest energy absorption and highest energy emission bands coincide, there are further electronic transitions which are unique to either absorption or emission. The energy difference between the maxima in the broad emission and absorption spectra, ca. 1920 cm⁻¹, is therefore not solely related to vibrational energies, but also to the locations of the relevant 5d¹ and 4f¹ electronic states.

The D₂ lamp and 355 nm excited luminescence spectra of Ce³⁺/Cs₂NaYCl₆ at 10 K are similar to the 199.8 nm excited spectrum, except that the highest energy bands are strongly self-absorbed. The 199.8 nm excited emission spectrum of Ce³⁺ doped into Cs₂LiYCl₆ is generally similar to, but less well-resolved than, the spectrum of Ce³⁺/Cs₂NaYCl₆ (Figure 5). The vibrational progression frequencies are given in column 4 of Table 4, and the derived energies are listed in column 4 of Table 5.

²E_g 5d¹–4f¹ Emission Spectra. Under 199.8 nm excitation at 10 K, a group of bands is observed in the emission spectrum of neat Cs₂NaErCl₆ which cannot be associated with electronic transitions of Er³⁺ (Figure 6). We tentatively assign this emission to the Ce³⁺ 5d¹ ²E_g state emitting to the 4f¹ electronic levels. The reasons for this assignment are because (i) the luminescence is clearly d-f and not f-f, and there are no f¹⁰d energy levels of Er³⁺ at such low energy; (ii) f-f luminescence from Er³⁺ would be quenched by the ⁴D_{1/2} state, just below 47 000 cm⁻¹; and (iii) the line intervals cannot be matched with energy level intervals of ErCl₆³⁻. Furthermore, these bands are evident neither in the emission spectrum of dilute Er³⁺/Cs₂NaYCl₆ nor in the 218 nm excited spectra of Cs₂NaErCl₆. The electronic origin at highest energy is located at 47 080 cm⁻¹ (Figure 6). The progressions in vibrational modes of 49 cm⁻¹ and 297 cm⁻¹ are characteristic of the 5d–4f emission spectra described above and are given in column 4 of Table 4. At the second member of the ν_1 progression, there is an apparent doubling of bands, which can be explained by the presence of a further electronic state at 594 cm⁻¹ above the ground state. It is for these reasons that we believe these bands can be assigned to emission from the d¹ ²E_g Γ_8 state of a Ce³⁺ impurity in neat Cs₂NaErCl₆.

Only one further similar group of bands is observed to lower energy. For this weaker group of bands (Figure 6), two further electronic origins can be assigned. The inferred locations of the 4f¹ ²F_{7/2} states (Table 5) are, however, rather lower (by about 40 cm⁻¹) than expected from the energy levels of Ce³⁺/Cs₂NaYCl₆. The derived energy levels are given in column 5 of Table 5.

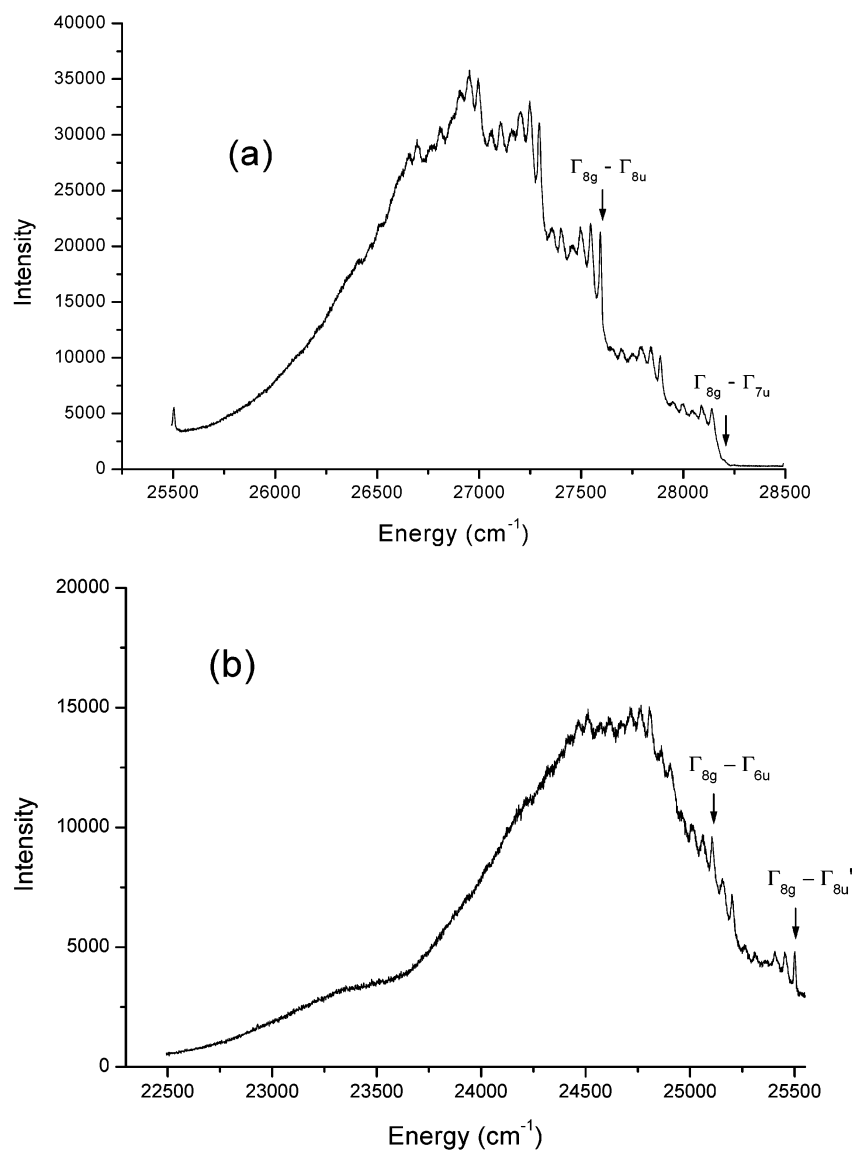
Since the 199.8 nm excitation energy is 2954 cm⁻¹ to the high energy of the highest energy zero phonon line of Ce³⁺, it appears that either the absorption takes place into an Er³⁺ energy level, with subsequent energy transfer to Ce³⁺ or cooperative ion effects occur. Strong emission from the 4f energy levels of Er³⁺ is observed at lower energies, which masks the ²T_{2g} Ce³⁺ transitions, if present.²⁴

We have assigned the fluorescence spectra observed in Cs₂NaErCl₆ beginning at 47 080 cm⁻¹ as the emission from the highest 5d¹ E_g level to the 4f levels of the Ce³⁺ ion. This assignment is consistent with other observations for the Ce³⁺ ion in this energy range as discussed in the Introduction. The observed vibronic spectra and the derived 4f energy levels given in Table 1 support this assignment. However, no fluorescence from the E_g state was observed in the Ce³⁺/Cs₂NaYCl₆

Table 4. Progression Frequencies and Bond Length Changes in f → d Transitions of Ce³⁺ in Elpasolite Lattices

crystal host	Ce ³⁺ concn (mol %)	transition	ν_1 (cm ⁻¹)	$\Delta Q(\nu_1)$ (Å) Ce–Cl	$\Delta r(\nu_1)^a$ (Å)	$\nu(\text{lat})$ (cm ⁻¹)	$\Delta Q(\text{lat})$ (Å) Ce–Cs	$\Delta r(\text{lat})^a$ (Å)
Emission								
Cs ₂ NaYCl ₆ <i>b</i>	0.5	$^2T_{2g} \Gamma_{8g} \rightarrow ^2F_{5/2} \Gamma_{8u}$	300 ± 2	0.12	0.050	48 ± 2	0.14	0.050
		$^2T_{2g} \Gamma_{8g} \rightarrow ^2F_{5/2} \Gamma_{7u}$	298 ± 3	0.11	0.046	48 ± 2	0.14	0.050
		$^2T_{2g} \Gamma_{8g} \rightarrow ^2F_{5/2} \Gamma_{8u}, \Gamma_{7u}$	299	0.09	0.037	47.5	0.139	0.049
Cs ₂ LiYCl ₆	1.0	$^2T_{2g} \Gamma_{8g} \rightarrow ^2F_{5/2} \Gamma_{8u}$	303 ± 2	0.11	0.043	54 ± 3	0.18	0.062
		$^2T_{2g} \Gamma_{8g} \rightarrow ^2F_{5/2} \Gamma_{7u}$	301 ± 1	0.12	0.049	52 ± 3	0.15	0.053
Cs ₂ NaErCl ₆ <i>b</i>		$E_g \rightarrow ^2F_{5/2} \Gamma_{7u}$	297 ± 5	0.10	0.040	49 ± 3	0.15	0.055
		$E_g \rightarrow ^2F_{5/2} \Gamma_{8u}, \Gamma_{7u}$	297	0.085	0.035	48	0.133	0.047
Absorption								
Cs ₂ NaYCl ₆	0.01	$^2F_{5/2} \Gamma_{7u} \rightarrow ^2T_{2g} \Gamma_{8g}$	299 ± 2	0.13	0.051	44 ± 3	0.15	0.054
Cs ₂ LiTmCl ₆		$^2F_{5/2} \Gamma_{7u} \rightarrow ^2T_{2g} \Gamma_{8g}$	296 ± 5			54 ± 3		
Cs ₂ LiPrCl ₆		$^2F_{5/2} \Gamma_{7u} \rightarrow ^2T_{2g} \Gamma_{8g}$	285 ± 5	0.13	0.051	51 ± 2	0.19	0.067

^a Absolute values of bond length difference between the 4f and 5d states involved in the particular transition. ^b Results from the Huang–Rhys analysis (see text).

**Figure 3.** (a,b) Xenon lamp excited UV emission spectrum (10 K) of Ce³⁺/Cs₂NaYCl₆ between 28 500 and 22 500 cm⁻¹.

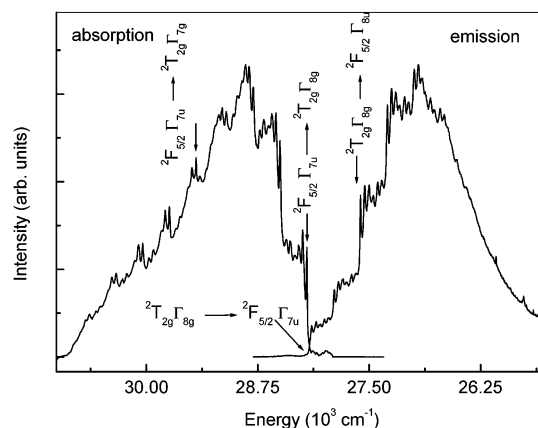
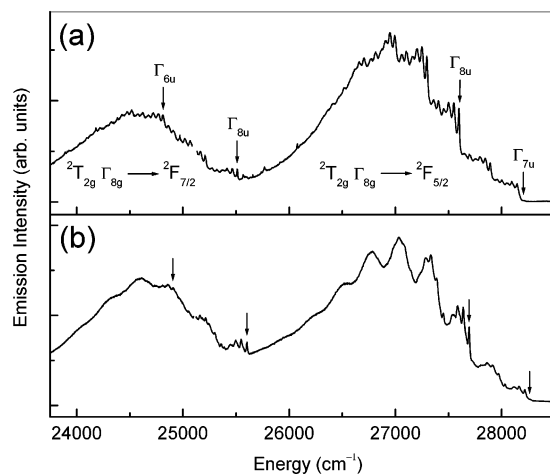
system when this system was excited in the wavelength range of 192–210 nm at 10 K, although T_{2g} emission was observed. The calculated E_g emission intensities are in poor agreement with the experimental data (see below). One possibility for the quenching of the E_g emission

in the Ce³⁺/Cs₂NaYCl₆ system is by 5d–5d energy transfer to killer sites. The most likely candidates are Pr³⁺ and/or Nd³⁺ since these ions have 5d levels in the 200 nm region. Analysis of the undoped Cs₂-NaYCl₆ crystal shows that these ions are present in relatively significant

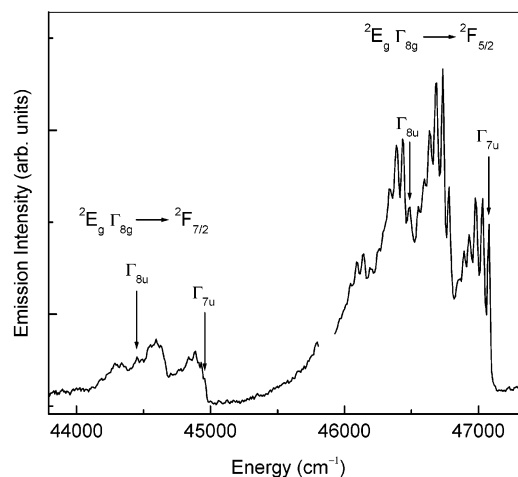
Table 5. Derived f and d Electron Energy Levels from the 10 K Emission and Absorption Spectra of CeCl_6^{3-}

state $n\ell$ ($2S+1$) L_J	irrep.	$\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$		$\text{Ce}^{3+}/$	calcd levels ^{a-c} (cm^{-1})
		$\text{Cs}_2\text{NaYCl}_6$ (cm^{-1})	$\text{Cs}_2\text{LiYCl}_6$ (cm^{-1})	$\text{Cs}_2\text{NaErCl}_6$ (cm^{-1})	
$4f^1\ 2F_{5/2}$	Γ_{7u}	0	0	0	0
	Γ_{8u}	599 ± 3	578	594	597
$4f^1\ 2F_{7/2}$	Γ_{7u}			2125	2167.
	Γ_{8u}	2689 ± 3	2674	2628	2691
	Γ_{6u}	3086 ± 3	3061		3085
$5d^1\ T_{2g}$	Γ_{8g}	$28\ 193 \pm 2$	$28\ 265 \pm 3$		28 196
	Γ_{7g}	29 435			29 435
$5d^1\ E_g$	Γ_{8g}			47 080	47 125

^a Data from $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$. For the $5d^1$ configuration, the Γ_{7g} level was taken from Schwartz and Schatz,⁹ and the Γ_{8g} level, from the $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ data. ^b Parameters (cm^{-1}) $4f^1$: $\zeta_{4f} = 624.1$, $B_0^4 = 2208.$, $B_0^6 = 249.6$. $5d^1$: $F^0 = 36\ 015.4$, $\zeta_{5d} = 792.7$, $B_0^4 = 38\ 709$. ^c $g(\Gamma_{7u})$ (calcd) = 1.253.

**Figure 4.** Comparison of 10 K absorption spectrum of $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ with the 199.8 nm excited emission spectrum at 10 K.**Figure 5.** Comparison of 199.8 nm excited 10 K emission spectra of (a) $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ and (b) $\text{Ce}^{3+}/\text{Cs}_2\text{LiYCl}_6$. The terminal f-electron states are labeled.

concentrations, so this is a possibility. Reliable analytical data could not be obtained for the Er_2O_3 starting material used to prepare $\text{Cs}_2\text{NaErCl}_6$. If the amount of Pr/Nd in the $\text{Cs}_2\text{NaErCl}_6$ crystal is significantly less than that in the $\text{Cs}_2\text{NaYCl}_6$ system, then this could be a possible explanation for the appearance of the $5d^1\ E_g$ emission. The fluorescence from the $\text{Ce}^{3+}\ E_g$ state is unlikely to be quenched by Er^{3+} f electron levels. Quenching by d electron levels of $\text{Nd}^{3+}/\text{Pr}^{3+}$ would not give rise to d–f emission from these lanthanide ions because Nd^{3+} does not exhibit d–f emission in elpasolites, and Pr^{3+} d – f

**Figure 6.** Emission spectrum (199.8 nm excited, 10 K) of $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ between 47 100 and 43 500 cm^{-1} .

emission is quenched by Ce^{3+} . Also, we have been unable to find another plausible mechanism.

Vibrational Progressions, Line Widths, and Condon Parabolaes.

Several vibrational progressions have been identified above in the $2T_{2g}\ 5d^1 - 4f^1\ 2F_{5/2}, 2F_{7/2}$ emission and absorption spectra of CeCl_6^{3-} . Selection rules for these spectra show that the vibrational mode must transform as the totally symmetric representation at the O_h crystal site of Ce^{3+} . Following the remarks of Schwartz and Schatz,⁹ and by comparison of the progression intervals with Table 2, it is clear an alternative, the occurrence of Jahn–Teller effects, is not evident in the $2T_{2g}$ state. These authors assigned vibrational progression modes with energies of 16 and/or 32 cm^{-1} . The first of these energies is comparable with the S_3 rotatory mode, whereas the second energy could correspond to an acoustic mode. The occurrence of progressions in these modes would thus infer contributions to the intensity from points away from the zone center. Since these progressions are not well-resolved, and we do not observe corresponding features in the spectra of $\text{Ce}^{3+}/\text{Cs}_2\text{LiLnCl}_6$, we do not discuss these bands further. The strongest progressions in the spectra of $\text{Ce}^{3+}/\text{Cs}_2\text{ALnCl}_6$ ($A = \text{Na}, \text{Li}$) occur in the ν_1 (α_{1g}) CeCl_6^{3-} moiety (i.e., first shell) mode, with the energy rather greater than that in neat $\text{Cs}_2\text{ACeCl}_6$ because CeCl_6^{3-} is compressed in the crystalline hosts employed. The next prominent progression occurs in the mode near 44–49 cm^{-1} in $A = \text{Na}$ hosts, but in 51–54 cm^{-1} in $A = \text{Li}$ hosts. Clearly the energy of this mode is not very sensitive to the masses of Ln or A, but it is similar to that of the S_5 (τ_{2g}) mode. This progression mode can therefore be envisaged as a $\mathbf{k} \neq 0$ totally symmetric mode (such as along the Δ direction of reciprocal space) or more simply (but less accurately) as the totally symmetric stretch of the second shell, CeCs_8 .

It is evident that a further, weaker progression occurs in a vibrational mode of 180–193 cm^{-1} for $A = \text{Na}$ and 237–252 cm^{-1} for $A = \text{Li}$. This vibration can be envisaged as the contribution from the S_8 (τ_{1u}) mode away from the zone center or, alternatively, from the totally symmetric stretch of the third shell, Ce–Na_6 . In all of these totally symmetric breathing modes, the Ce nucleus is stationary. Additional evidence for this latter “sodium” mode comes from the study of the line widths and relative intensities of consecutive bands in the emission spectra. When the emission transition $2T_{2g}\ \Gamma_{8g} \rightarrow 2F_{5/2}\ \Gamma_{8u}$ is considered, after subtraction of the continuous background, the first few bands can be better fitted by Gaussian rather than Lorentzian profiles (Figure 7). This is presumably because some of the fitted bands comprise more than one component. The half-height width shows an increase for the first few bands in the progression of the 48 cm^{-1} lattice mode, with a progressive decrease in intensity. A sharper feature is then apparent at $190 \pm 3\ \text{cm}^{-1}$, which must then correspond to the first member of a further progression. The lowest energy band in Figure 7 corresponds

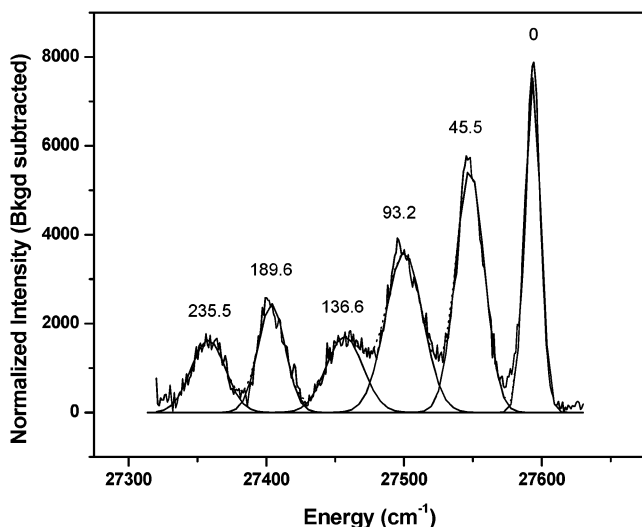


Figure 7. Gaussian fits to the first few bands in the 10 K ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$ emission spectrum of $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$. The numbers over the centers of the bands indicate the energy intervals (in cm^{-1}) from the zero phonon line.

to the first member of the 48 cm^{-1} lattice mode progression upon the 190 cm^{-1} mode.

The wave functions obtained from eq 1 represent only the pure electronic wave functions. When vibronic coupling is also considered, the intensity of an electronic transition from the initial state i to the final state f may be written (in the adiabatic approximation which assumes the electronic part is independent of the vibrational coordinates) as

$$I \propto |\langle i | e \mathbf{r} | f \rangle \langle l | m \rangle|^2 \quad (2)$$

where I is the intensity, $e \mathbf{r}$, the electric dipole operator, and l and m are the initial and final vibrational states, respectively.^{38,39} If it is further assumed that the electronic–vibrational coupling is linear (i.e., the vibrational states in the ground and excited states are equal) and only the lowest vibrational level of the initial state is populated, then

$$I_n \approx e^{-S_{H-R}} \left(\frac{S_{H-R}^n}{n!} \right) \quad (3)$$

where S_{H-R} is the Huang–Rhys parameter and n is the vibrational quantum number of the terminal state.

The Huang–Rhys parameter can be evaluated from a harmonic progression in a vibrational mode. For the vibration corresponding to the normal coordinate Q_i ,

$$S_{H-R} = \frac{M \omega_i}{2\hbar} (\Delta Q_i)^2 \quad (4)$$

where M is the effective mass and ΔQ_i is the difference between the equilibrium distances of the metal ion and the ligand in the ground and excited states for the vibrational mode ν_i of angular frequency ω_i .^{38,39}

A similar method to relate the change in intensity along a vibrational progression to the change along the corresponding vibrational coordinate has been given by Yersin et al.⁴⁰ They have related the measured, relative vibronic intensities in emission $I^{0,n}$ and absorption $I^{m,0}$ (where m, n indicate the number of quanta) to the zero phonon

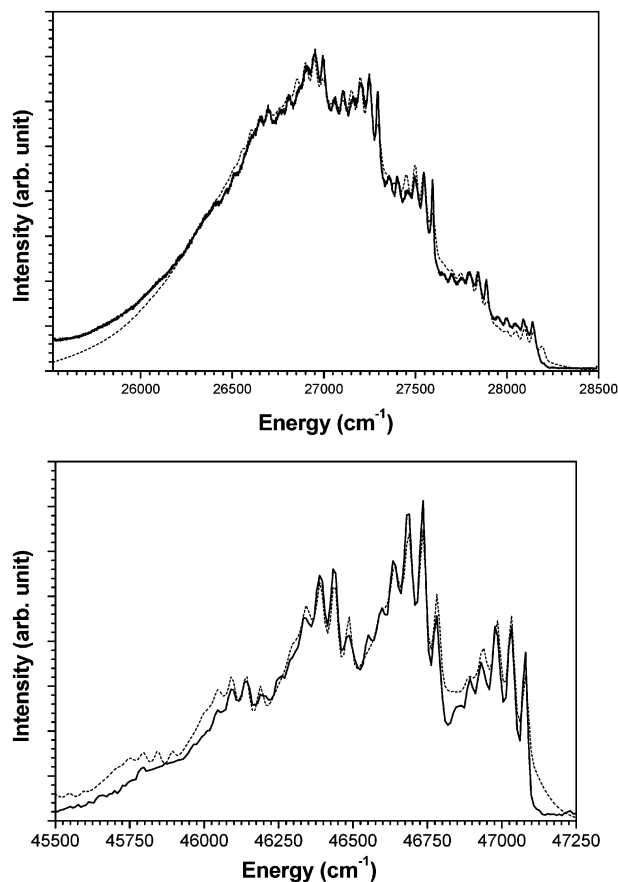


Figure 8. Fits of the experimental emission spectra using the Huang–Rhys formulation as described in the text. (Top) $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$: $S_{H-R1} = 1.275$, $\nu_1 = 299 \text{ cm}^{-1}$, line width = 14 cm^{-1} ; $S_{H-R2} = 1.8$, $\nu_{\text{lat}} = 47.5 \text{ cm}^{-1}$, line width = 14 cm^{-1} ; $S_{H-R3} = 4.39$, $\nu_{\text{bkgd}} = 202 \text{ cm}^{-1}$, line width = 145 cm^{-1} ; intensity ratio of the transitions ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$ to ${}^2T_{2g} \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u} = 2.0$. (Bottom) $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$: $S_{H-R1} = 1.13$, $\nu_1 = 297 \text{ cm}^{-1}$, line width = 9 cm^{-1} ; $S_{H-R2} = 1.3$, $\nu_{\text{lat}} = 48 \text{ cm}^{-1}$, line width = 9 cm^{-1} ; $S_{H-R3} = 1.55$, $\nu_{\text{bkgd}} = 300 \text{ cm}^{-1}$, line width = 105 cm^{-1} ; intensity ratio of the transitions $E_g \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$ to $E_g \Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u} = 0.13$. The calculated spectra are shown as the dotted lines, the experimental data are shown as solid lines. Gaussian line shapes are assumed.

line (ZPL) intensity, $I^{0,0}$. For the case of the ν_1 progressions,

$$\frac{I^{0,n}}{I^{0,0}} = \left[\frac{E(\text{ZPL}) - n\nu_1}{E(\text{ZPL})} \right]^4 \left[\frac{R_{0,n}}{R_{0,0}} \right]^2 \quad (5a)$$

$$\frac{I^{m,0}}{I^{0,0}} = \left[\frac{E(\text{ZPL}) + m\nu_1}{E(\text{ZPL})} \right]^2 \left[\frac{R_{m,0}}{R_{0,0}} \right]^2 \quad (5b)$$

where the overlap integrals $R_{0,n}$ and $R_{m,0}$ can be related to the displacement ΔQ of the minimum of the potential surface of the excited electronic state along the α_{1g} normal coordinate. Furthermore, the individual Ce–Cl bond length change is $\Delta r = \Delta Q/\sqrt{6}$. The Franck–Condon analyses were performed upon the emission and absorption spectra, after subtraction of the continuous background.⁴¹

The spectra shown in Figure 8 were fit by using the Huang–Rhys formulation for three oscillators, S_{H-R1} corresponding to the $\sim 300 \text{ cm}^{-1}$ ν_1 vibration, S_{H-R2} corresponding to the $\sim 48 \text{ cm}^{-1}$ assigned to the totally symmetric stretch ν_{lattice} vibration. The third frequency S_{H-R3} was used to fit the broad background. The line widths were treated as free parameters, and the relative intensities of the two electronic transitions involved, ${}^2T_{2g}$ (or E_g) $\Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{7u}$ and ${}^2T_{2g}$ (or E_g) $\Gamma_{8g} \rightarrow {}^2F_{5/2} \Gamma_{8u}$, were adjusted to give the best fit. Representative fits for the ~ 28000

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Table 6. Relative Experimental and Calculated Electric Dipole Emission Intensities for CeCl_6^{3-}

	relative fluorescence intensity from $5d^1 T_{2g} \Gamma_{8g}^a$ exptl	relative fluorescence intensity from $5d^1 T_{2g} \Gamma_{8g}$ calcd	relative fluorescence intensity from $5d^1 E_g \Gamma_{8g}^b$ exptl	relative fluorescence intensity from $5d^1 E_g \Gamma_{8g}$ calcd
$4f^1 {}^2F_{5/2} \Gamma_{7u}$	0.2	0.76	1.0	1.0
$4f^1 {}^2F_{5/2} \Gamma_{8u}$	1.0	1.0	0.2	6.9
$4f^1 {}^2F_{7/2} \Gamma_{7u}$		0.03	0.15	1.5
$4f^1 {}^2F_{7/2} \Gamma_{8u}$	0.05	0.33	0.05	8.2
$4f^1 {}^2F_{7/2} \Gamma_{6u}$	0.2	0.30		5.3

^a $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$. ^b $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$.

cm^{-1} emission of $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$ (from Figure 3a) and for the $\sim 48\,000\text{ cm}^{-1}$ emission of $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$ (from Figure 6) are shown in Figure 8.

Franck–Condon analyses using eqs 5a and 5b also were performed upon all the emission and absorption spectra, after subtraction of the continuous background⁴¹ assuming that the vibrational frequencies are unchanged in the ground and excited states.

The derived parameters, Δr and ΔQ , are listed in columns 5 and 6 for the Ce–Cl bonds and columns 8 and 9 of Table 4 for the Ce–Cs bonds. The displacement between the d and f electron potential energy hypersurfaces of $0.09\text{--}0.13\text{ \AA}$ represents a Ce–Cl bond length change of about 0.04 \AA , which is $<2\%$ of the bond length. Similar changes have been obtained from the analysis of $5d \rightarrow 4f$ emission transitions of Pr^{3+} in elpasolite lattices.⁴² The bond length change along the Cs^+ lattice mode coordinate from this analysis is $0.05\text{--}0.07\text{ \AA}$.

A similar fit was performed for the $\sim 50\,000\text{ cm}^{-1}$ emission assigned (tentatively) as due to the ${}^2E_g \Gamma_8 \rightarrow {}^2F_{5/2}$. With this initial state, the displacement between the d and f electron potential energy hypersurfaces is $0.08\text{--}0.09\text{ \AA}$, representing a Ce–Cl bond length change of about 0.035 \AA , slightly smaller than found with the ${}^2T_{2g} \Gamma_8$ as the initial state. The differences in bond distances found for transitions that are initiated from either the T_{2g} or the E_g orbitals can be rationalized by the differences in bonding in these two $5d$ orbitals (see below).

Electric Dipole Intensities and Crystal Field Calculations. The wave functions obtained from diagonalization of the matrices given by eq 1 can be used to evaluate eq 2. The radial part of eq 2 is the same for all transitions, so we compare the calculated relative intensities with the measured relative intensities for the emission transitions in Table 6.

The measured electric dipole intensities from the $T_{2g} \Gamma_8$ state to the $4f$ levels were obtained by subtracting an empirical background corresponding to the underlying broad background shown in Figure 3 from the spectra and then fitting the vibronic peaks with a Gaussian peak-fitting program. We estimate the accuracy of the experimental intensities obtained in this way to be about 50%. For transitions originating from the lowest level of the $5d^1$ configuration, the agreement between the experimental and calculated relative intensities is reasonable.

With the assumption that Figure 6 corresponds to emission from the 2E_g state of Ce^{3+} , then the relative intensities of transitions from this level are not in good agreement with calculation. This is not because the lower energy bands are absorbed by Er^{3+} transitions in $\text{Cs}_2\text{NaErCl}_6$, since there is a spectral window between $44\,000$ and $46\,000\text{ cm}^{-1}$ for the energy levels of Er^{3+} .

The calculated intensities show that the emission to the $4f^1 {}^2F_{7/2}$ states should be considerably greater from the $5d^1 E_g$ levels than from the $5d^1 T_{2g}$ levels. The reason for this intensity change is because only transitions with $\Delta J = 0, \pm 1$ are allowed. The $5d^1 E_g$ wave functions have $\sim 65\%$ $L = 3, J = 5/2$ character and $\sim 35\%$ $L = 3, J = 3/2$ character as compared to the $\sim 35\%$ $L = 3, J = 5/2$ character and $\sim 65\%$ $L = 3, J = 3/2$ character of the $5d^1 T_{2g}$ wave functions. Thus, for the $5d^1 T_{2g}$

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Table 7. Ab Initio Embedded Cluster Calculations on $\text{Cs}_2\text{NaYCl}_6:(\text{CeCl}_6)^{3-}$

main character	state	$r(\nu_1)$ (\AA)	$\Delta r(\nu_1)$ (\AA)	ν_1 (cm^{-1})	T_g^a (cm^{-1})	exptl zero-phonon levels (cm^{-1})
$4f^1 {}^2F_{5/2}$	Γ_{7u}	2.723	0	305	0	0
	Γ_{8u}	2.727	0.004	307	831	596^b
	Γ_{7u}	2.724	0.001	307	2318	2125^c
$4f^1 {}^2F_{7/2}$	Γ_{8u}	2.727	0.004	307	3019	2686^b
	Γ_{6u}	2.727	0.004	307	3376	3083^b
	Γ_{8g}	2.676	-0.047	293	25510	$28\,195^b$
$5d^1 {}^2T_{2g}$	Γ_{7g}	2.676	-0.047	293	26716	$29\,435^{b,d}$
	Γ_{8g}	2.740	0.017	297	47263	$47\,080^c$

^a Minimum-to-minimum energy differences. ^b In $\text{Ce}^{3+}/\text{Cs}_2\text{NaYCl}_6$. ^c In $\text{Ce}^{3+}/\text{Cs}_2\text{NaErCl}_6$. ^d From Schwartz and Schatz.⁹

wave functions, the major component of the wave functions cannot contribute any intensity (in the limit of zero crystal field mixing) to the $4f^1 J = 7/2$ levels. Nevertheless, the experimental intensities from the $5d^1 E_g$ levels are completely off from the calculated values. In fact, the calculated values show the intensities to the $4f^1 J = 7/2$ states should be larger than to the $4f^1 J = 5/2$ states, completely in reverse to the observed values.

As expected, the crystal field fits shown in Table 5 agree with the experimental energies quite well. In this case, the number of observables and the number of parameters are comparable. A better test is the comparison of the calculated ground state $4f^1 \Gamma_{7u} g$ value, $g = -1.253$, with the experimental value, $g = |1.266|$.¹⁰

Ab Initio Calculations. To complement the data with independent theoretical information, we performed wave function based ab initio calculations on the $(\text{CeCl}_6)^{3-}$ cluster embedded in a reliable representation of the $\text{Cs}_2\text{NaYCl}_6$ host. The results are summarized in Table 7. These calculations take into account the most important bonding interactions within the $(\text{CeCl}_6)^{3-}$ unit, including electron correlation and scalar and spin–orbit coupling relativistic effects, and $\text{Cs}_2\text{NaYCl}_6$ host embedding effects.

The details of the calculations follow. We use the ab initio model potential method, AIMP, as an embedding technique and as an effective core potential method.^{20,21} The embedding potential we use for $\text{Cs}_2\text{NaYCl}_6$ was obtained earlier.⁴³ The relativistic AIMP we use for Ce was obtained from Seijo⁴⁴ and represents its [Kr] core; the ab initio spin–orbit potential produced earlier⁴⁵ is used here with an empirical scaling factor 0.9;⁴⁶ the basis set for the $4d5s5p4f5d$ valence is the (14s10p10d8f)/[6s5p6d4f] set.⁴⁴ For Cl, we use the [Ne] core AIMP and the (7s6p) basis set⁴⁷ extended with one diffuse p function⁴⁸ and contracted as [3s4p]. Additional (7s4p)/[1s1p] basis set functions are located on the Na^+ ions along the 100, 010, and 001 directions that are next neighbors to the $(\text{CeCl}_6)^{3-}$ cluster.⁴³ The electron correlation effects from the 36 3p electrons of the Cl ligands and the unpaired electron of Ce^{3+} are included by means of average coupled pair functional calculations, ACPF.^{49,50} Finally, we use the spin-free-state-shifted spin–orbit Hamiltonian (sfss)⁵¹ in an identical manner as that described⁵² for $(\text{PaCl}_6)^{2-}$, to put together the electron correlation effects and the spin–orbit coupling effects in a simplified way.

The calculated bond distances along the breathing mode are shown in column 3 of Table 7. They are almost equal for all the states of the

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4f¹ manifold; the slightly smaller values for the two Γ_{7u} states correspond to those being the only ones with 4f(a_{2u}) orbital character, which is the f orbital most stabilized by the ligand field. All these states have essentially the same ν_1 vibrational frequency (column 5, Table 7). The computed values compare well with the experimental data. The computed minimum-to-minimum energy differences of the potential energy surfaces (corresponding to the zero phonon experimental energies) listed in column 6 of Table 7) are very reasonable when compared with experiment (column 7 of Table 7). To lower the mean average deviation from 260 cm⁻¹, it would probably be necessary to increase the methodological and computational demands to a very large extent. A more detailed analysis of these differences shows that its main contribution comes from a slight excess stabilization of the 4f-(a_{2u}) molecular orbital (e.g., the mean average deviation from experiments is 80 cm⁻¹ for the Γ_{8u} and Γ_{6u} states, with no 4f(a_{2u}) contribution) which indicates that these calculations may be slightly overestimating the effective ligand field.

The calculations on the 5d¹ manifold are perhaps more interesting. The bond distance of the two ²T_{2g} states, Γ_{8g} and Γ_{7g} , are the same and smaller than the bond distance of the 4f¹ states. The absolute value of the offset, 0.047 Å, shown in column 4 of Table 7 agrees well with the experimentally deduced value in Table 4. The fact that it is negative could not have been deduced from the analysis of the emission band shapes, which leads only to absolute values. The prediction of a cluster contraction in the transition from 4f to 5d(t_{2g}) was also made in the corresponding case⁵² of Pa⁴⁺; it has to be the result of a balance between opposite tendencies: to increase bond distance as a consequence of the larger size of the 5(6)d orbital, on one hand, and to reduce bond distance as a consequence of the larger bond covalency in the 5(6)d¹ states, on the other. An analysis of the detailed reasons leading to this contraction has been presented elsewhere.⁵³ The bond distance of the 5d¹ ²E_g Γ_{8g} is larger than that of the ²T_{2g} states, as usual for the O_h ligand field splitting of d states and corresponding to the 5d(e_g) orbital being destabilized with respect to the 5d(t_{2g}). The bond distance increases so as to make it larger than the 4f¹ bond distances by 0.017 Å (column 4, Table 7). The calculated vibrational frequencies are very similar to the 4f¹ ones, only very slightly smaller, and they are again close to the approximate experimental value of 300 cm⁻¹ deduced from absorption and MCD spectra of Ce³⁺/Cs₂NaYCl₆. The minimum-to-minimum potential energy surface energies from the ground state to the two ²T_{2g} states, Γ_{8g} and Γ_{7g} , are 2700 cm⁻¹ too low, which is a reasonable result for a theoretically demanding 4f → 5d transition. Finally, the energy of the 5d¹ ²E_g Γ_{8g} state is calculated to be 47 260 cm⁻¹. It agrees extremely well with the experimental observation in Ce³⁺/Cs₂NaErCl₆, very probably as a consequence of compensation between an underestimation of the 4f → 5d baricenter and an overestimation of the ligand field, as already observed in the splitting of the 4f¹ manifold. In any case, the ab initio calculation strongly suggests the existence of the 5d¹ ²E_g Γ_{8g} state of the (CeCl₆)³⁻ unit 46 000–48 000 cm⁻¹ above the ground state. This independent result supports the assignments of the emission spectrum of Ce³⁺/Cs₂NaErCl₆ in Figure 6.

Discussion and Conclusions

In this paper, we have reported the results of detailed spectroscopic investigations of the Ce³⁺ ion in chloroelpasolite hosts. The complete energy level schemes for the 4f¹ and 5d¹ configurations may be inferred from a combination of the fluorescence and absorption data from our work with earlier absorption data. Good fits were obtained for both the 4f and 5d levels using the crystal field model. However, although the calculated emission intensities from the 5d T_{2g} Γ_8 level were in reasonable agreement with the experimental intensities, the calculated intensities from the 5d E_g Γ_8 level were completely off. It is

possible that admixtures of charge transfer states into the 5d E_g state could be important. We have tentatively assigned the energy of the upper 5d¹ E_g level (47 080 cm⁻¹) for the Ce³⁺ ion from the observed UV emission in a Cs₂NaErCl₆ crystal at low temperatures. Further experiments are needed in order to conclusively prove this assignment. Unfortunately, at this time, we do not have the necessary facilities to perform excitation or lifetime measurements in this spectral region.

Theoretical calculations are presented which give reasonable agreement with the experimental energy levels and support the assignment of the 47 080 cm⁻¹ feature to the 5d¹ E_g level. These calculations also show that the change in bond length between the 4f¹ and 5d¹ T_{2g} configuration is contractive with a value of ~0.04 Å, in excellent agreement with the experimental result (note that only the absolute value is obtained from the experimental results). This short bond for the 5d T_{2g} state suggests that the covalency of this 5d orbital with its consequent bond length shortening outweighs the lengthening of this bond due to the larger size of the 5d orbital. A detailed analysis for this has been presented elsewhere.⁵³ By contrast, the experimental measurements from the E_g emission spectrum show a slightly smaller bond length change than that for the T_{2g} state. The theoretical calculations predict an increase in this bond length relative to that in the ground 4f configuration, which means a smaller bond length change than that obtained from the experimental analysis.

One factor that can account for some of these discrepancies hinges upon the subtraction of the broad background when integrating peaks in the emission or absorption spectra. Rather different results are obtained if the entire vibronic sideband is integrated (for example, in the Figure 4 absorption spectrum, the maximum is at $n = 1$ if individual bands are considered but at $n = 2$ quanta of ν_1 if the background is not subtracted). Although fits also were made assuming the background could be reproduced as a Gaussian function or by reproducing the background with a band coming from the Huang–Rhys equation with an empirical width, this may not necessarily account for the entire background. For example, (i) there are overlapping electronic transitions in some cases, and (ii) progressions in multiple quanta of odd vibrational modes may occur, partly giving rise to the broad underlying background. Furthermore, the relative intensities of the transitions involved with the 47 080 cm⁻¹ emission were in disagreement with the predicted relative intensities obtained for the allowed electric dipole calculations. Thus the relative measured intensities from which the bond length changes are obtained must be considered somewhat suspect.

Acknowledgment. This research was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 with the University of California. P.A.T. acknowledges financial support for this study from the Hong Kong University Grants Commission Research Grant City U 1098/01P. L.S. and Z.B. acknowledge financial support from Ministerio de Ciencia y Tecnología, Spain (Dirección General de Investigación, BQU2002-01316). We are indebted to Dr. Kwok Wai-Ming for recording the 199.8 nm emission spectrum and to Dr. D. L. Phillips for the use of his laser laboratory. We also wish to thank Dr. M. F. Reid for performing the 5d–4f intensity calculations reported in this paper.

JA036659X

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