

# Simulated Infrared Spectra of Ho(III) and Gd(III) Chlorides and Carboxylate Complexes Using Effective Core Potentials in GAMESS

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The mid- and far-infrared spectra of Ho(III) and Gd(III) chloride hexahydrate, anhydrous Gd(III) formate, Ho(III) and Gd(III) acetate hemihydrate and trihydrate, and Gd(III) benzoate monohydrate have been computed by the ROHF/SBKJC method in GAMESS. The calculated spectra successfully simulated the experimental spectra down to 50 cm<sup>-1</sup>. Absorptions due to coordinated water were distinguished from those due to O–C–O bending in chelate rings. The number of water molecules bound to Ln(III) in a complex was successfully predicted from the match of the experimental spectra to the simulated Ln–O vibrations in the far IR.

## INTRODUCTION

The modeling of lanthanide systems has grown recently, in response to the development of lanthanide-containing materials that capitalize on the magnetic properties of the 4f elements.<sup>1</sup> Lanthanide-doped polymer films are one example of a class of advanced materials that could profit from the modeling of Ln(III) ions complexed within their chemical structures. These films could be potentially used as optically transparent, magnetic shields;<sup>2</sup> the purposeful design and synthesis of such materials could be aided through the computation of the far-infrared bands, which yield information about the coordination number and approximate geometry of the complexed site in the polymer.

The application of quantum methods to lanthanides has been surveyed, and the majority of calculations were found to employ effective core potentials (ECP) on molecules with small numbers of atoms.<sup>3</sup> Semiempirical methods have been applied to large lanthanide complexes;<sup>4,5</sup> however, an ab initio method would be required to precisely predict infrared frequencies. This paper reports the first effort to apply effective core potentials to models of large lanthanide complexes, and to convert the resultant simulated infrared modes to continuous line spectra.

Effective core potentials for lanthanides were first developed by Stevens and Cundari.<sup>6</sup> In this scheme, all inner core electrons through Kr[4d<sup>10</sup>] are replaced by a numerical potential that allows the modeling of lanthanide systems to become possible and economical. The lanthanides were modeled in the +3 oxidation state; however, the empty 6s<sup>2</sup> and 5d<sup>1</sup> orbitals were included in the valence space to provide for possible lanthanide–ligand interactions. The 5s and 5p electrons were also included in the valence space, in addition to the 4f electrons, to preserve accurate splittings of the atomic and ionic ground states.

Ho(III) and Gd(III) ions were used in this study to anticipate future modeling of magnetic materials that would require the high number of unpaired electrons and high

magnetic susceptibility these ions afford. The models were optimized under C<sub>1</sub> symmetry in a first attempt to demonstrate the ability to predict approximate geometry, type of coordination, and coordination number in complexes with unknown structure, as a long-term goal.

## COMPUTATIONAL METHODS

The calculations described in this paper use effective core potentials for lanthanide atoms with the RHF and ROHF methods in GAMESS.<sup>7</sup> Gradient-driven optimizations, starting from an unconstrained symmetry control of C<sub>1</sub>, and Hessian calculations were performed on 12 models of Ho(III) and Gd(III) chloride hydrates, 6 models of Ho(III) and Gd(III) acetates, 1 model of anhydrous Gd(III) formate, and 1 model of Gd(III) benzoate monohydrate. The GAMESS program resided on an SGI Origin 2000 computer, running on a scalar/sequential platform. Initially, all models were partially optimized with their lutetium homologues in order to generate reasonable molecular orbitals which were then applied to the Ho(III) or Gd(III) optimization file. The optimization tolerance was set to 1 × 10<sup>-5</sup> hartrees/bohr; typical run times for the chloride models (up to 25 atoms for the hexahydrates) averaged 15 days of CPU time. These run times represent cumulative CPU times from the initial lutetium file, the Ln(III) optimization file, and the Hessian file for each model. Similarly, models of the larger complexes (~40 atoms) averaged 35 days of CPU time.

The valence spaces for the Ln(III) ions are described by Gaussian type orbitals in the SBKJC basis.<sup>6</sup> All other atoms in the chloride models used a split valence, SV 6-31 basis. An all-electron 6-31G(d) basis set was used on all oxygen atoms in the models of the complexes.

The starting geometries for the model structures were obtained as follows. Models of the chlorides of the general formula, LnCl<sub>2,3</sub>·xH<sub>2</sub>O, were constructed with varying coordination numbers (C.N. 3–8) and charge by changing the number of water and chlorine ligands bonded to Ln(III). A starting geometry for Gd(III) chloride hexahydrate was taken

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from crystal coordinates reported by Couture et al.,<sup>8</sup> where the compound is known to occur mainly as a cationic species of C.N. 8,  $[\text{GdCl}_2 \cdot 6\text{H}_2\text{O}]^+$ .<sup>9,10</sup> All other initial geometries for the remaining chloride models used the Gd(III) hexahydrate model as a template, modifying the number of water and chlorine ligands as needed, with a subsequent minimization in Chemsite Unimolecular Visualizer.<sup>11</sup> Models of the acetates were constructed and minimized in Chemsite with the exception of the trihydrate model which used the structure of  $\text{Dy}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  as a template.<sup>12</sup> The models for the formate and benzoate complexes were also constructed and minimized in Chemsite.

The computed frequencies of the normal modes were scaled by a factor of 0.89; the use of scaling factors in SCF calculations is an accepted practice to offset the 10–12% error in frequency that occurs due to the small basis set used.<sup>13,14</sup> For all models, the simulated spectra were created by converting the band intensities and modified frequencies from the normal coordinate analysis to Gaussian band shapes using the Fortran program IRSIM.<sup>15</sup> This program was written in our laboratory and allows as many as 300 modes to be processed into an IR spectrum; the modes from each model were processed with a bandwidth of  $20\text{ cm}^{-1}$ . The output from IRSIM consists of numerical data; a continuous line spectrum was achieved by exporting the IRSIM.out file to the chart option in EXCEL.

## EXPERIMENTAL SECTION

Holmium and gadolinium trichloride hexahydrate, 99.99%, were obtained from Aldrich Chemicals. Analysis by Karl Fischer, Thermogravimetric Analysis (TGA), and Inductively Coupled Argon Plasma determined that there were between 5 and 6 waters of hydration for each formula unit of the compounds. Holmium and gadolinium acetate hemihydrate and trihydrate were also obtained from Aldrich Chemicals. The amount of water in each compound was confirmed by TGA to be 0.5 and 3 waters of hydration, respectively.

Mid- and far-IR spectra of the chlorides and acetates were acquired on a Nicolet Nexus 670 FT-IR instrument. Mid-IR spectra were collected on samples pressed into KBr pellets; the instrument was calibrated with polystyrene film and the spectra needed no correction. Far-IR spectra ( $600\text{--}50\text{ cm}^{-1}$ ) were collected using a DTGS detector/polyethylene window with a solid substrate silicon wafer as the beam splitter. The samples were milled with Nujol and smeared onto Parafilm. The far-IR absorptions recorded by the instrument were calibrated using  $\text{Cr}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ , and  $\text{Gd}_2\text{O}_3$  and corrected by  $+5\text{ cm}^{-1}$  in the range of  $225\text{--}200\text{ cm}^{-1}$ .<sup>16</sup> Outside this range, no correction to the measured frequencies was needed. The far-IR spectra of Ho(III) and Gd(III) chloride hexahydrate thus obtained agreed with the experimental spectra reported in the literature.<sup>17</sup> The mid- and far-IR spectra of the formate<sup>18,19</sup> and benzoate<sup>20,21</sup> complexes were found in the literature.

## RESULTS AND DISCUSSION

**1. Ho(III) and Gd(III) Chlorides.** These compounds were selected as the first test of the predictive ability of the ROHF/SBKJC method because the simplicity of the IR spectra

**Table 1.** Simulated Ln–Cl Vibrations Compared to Experiment

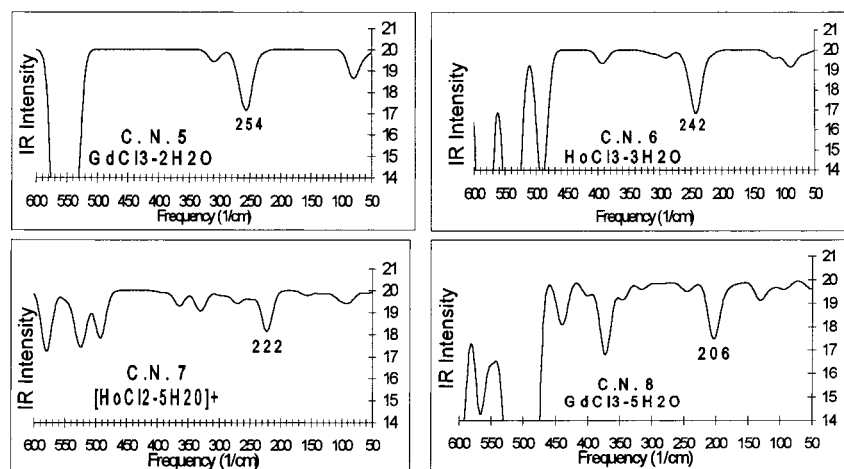
compound	C.N.	Gd–Cl ( $\text{cm}^{-1}$ )	Ho–Cl ( $\text{cm}^{-1}$ )
$\text{LnCl}_3 \cdot x\text{H}_2\text{O}^a$	not reported	221, 180–170	228, 200–196
$\text{LnCl}_3 \cdot 6\text{H}_2\text{O}^b$	7 and 8	219, 196	227, 199
<b>model</b>		<b>calculated modes</b>	
anhydrous $\text{LnCl}_3$	3	290	297
$[\text{HoCl}_2 \cdot 2\text{H}_2\text{O}]^+$	4		306
$\text{GdCl}_3 \cdot 2\text{H}_2\text{O}$	5	254	
$\text{HoCl}_3 \cdot 3\text{H}_2\text{O}$	6		242
$\text{GdCl}_3 \cdot 4\text{H}_2\text{O}$	7	205	
$[\text{LnCl}_2 \cdot 5\text{H}_2\text{O}]^+$	7	219	222
$\text{LnCl}_3 \cdot 5\text{H}_2\text{O}$	8	206	213
$[\text{LnCl}_2 \cdot 6\text{H}_2\text{O}]^+$	8	197	199

<sup>a</sup> Data comes from spectra of the Ho(III) and Gd(III) compounds reported in ref 17. <sup>b</sup> Aldrich samples were found to have between 5 and 6 waters of hydration in their compositions.

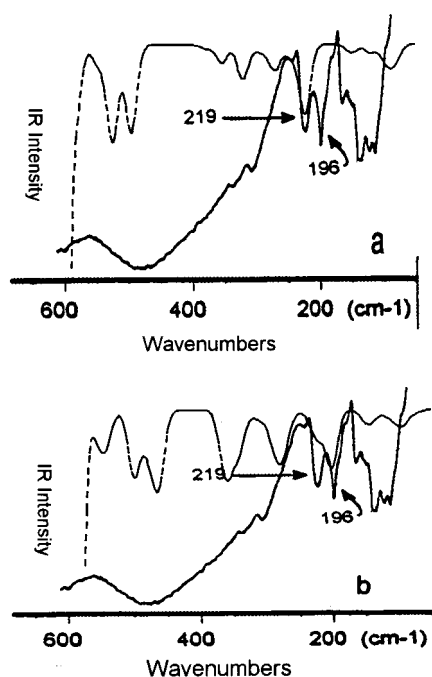
allows an easy assessment of the changes in number of bands and shifts of absorptions that result from changes in the coordination number of the model. Table 1 lists the Ln–Cl vibrations for the 12 models, compared to the experimental data of the far-IR spectra for the hexahydrate compounds. The vibrations were assigned from the normal coordinate analysis and clearly show that the frequency of the Ln–Cl absorption decreases as the number of bonds around the Ln(III) increases. Additionally, the number of absorption bands in each spectrum increased as the number of bonds increased, resulting in dramatic differences in the profiles of the simulated spectra as the C.N. of the models was varied (Figure 1). The distinct differences between the simulated spectra show that the ROHF/SBKJC method is sensitive to changes in molecular geometry, an important result since the ligands added or deleted in the models are identical. Table 1 also shows that, for the Ho(III) and Gd(III) homologues, the metal–chlorine stretching frequency is higher for holmium than for gadolinium. This prediction agrees with expectations and arises from the lanthanide contraction, where the shorter Ho–Cl interatomic distance results in a higher force constant for the bond, even though the mass of holmium is greater than that of gadolinium.

As a final demonstration of predictive ability, Figure 2 shows how the Gd–Cl absorptions from the simulated spectra of the cationic models of C.N. 7 ( $219\text{ cm}^{-1}$ ) and C.N. 8 ( $197\text{ cm}^{-1}$ ) exactly match both Gd–Cl absorptions in the experimental spectrum of Gd(III) chloride hexahydrate. After a survey of all the simulated spectra, only the spectra produced from these two models matched the experimental data. Furthermore, neither of the simulated spectra displayed both metal–chlorine bands found in the experimental spectrum that would indicate different Gd–Cl modes. Instead, these data lead to the conclusion that the compound is a mixture of cationic species, some with C.N. 7 and others with C.N. 8, and these conclusions are in agreement with the crystal data in the literature.<sup>9,10</sup> Finally, it should be noted that the cationic models of C.N.'s 7 and 8 contain 5 and 6 molecules of water, respectively. This corresponds to the water content in the commercial "hexahydrate" compounds, as determined by the analytical methods given in the Experimental Section. A survey of the simulated spectra for the holmium salt yielded the identical results.

The broadness of the bands due to water ( $480\text{ cm}^{-1}$  and  $120\text{ cm}^{-1}$ ) is not replicated in the simulated spectra because each model is only a single molecule and thus, does not take



**Figure 1.** Selected simulated spectra from the chloride models show dramatic changes when the coordination number in the models is varied.



**Figure 2.** Overlay of the experimental spectrum (continuous line) of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  onto the simulated spectra (dotted lines) of (a)  $[\text{GdCl}_2 \cdot 5\text{H}_2\text{O}]^+$ , C.N. 7 and (b)  $[\text{GdCl}_2 \cdot 6\text{H}_2\text{O}]^+$ , C.N. 8.

into account the hydrogen bonding between adjacent molecules that is actually present in crystalline Ln(III) chloride hydrates.

**2. Carboxylate Complexes.** The application of the ECP method to carboxylates demonstrated that (a) the mid- and far-IR spectra of carboxylates could be effectively simulated, (b) the chelate ring modes and water modes could be distinguished, and (c) the number of water groups in a carboxylate complex could be predicted correctly based on the frequencies of the far-IR bands. Each prediction is discussed separately below.

(a) Table 2 lists the simulated mid- and far-IR bands as well as the experimentally observed absorptions for the formate, acetate, and benzoate complexes of Ho(III) and Gd(III) and shows that many of the simulated frequencies are very close to, if not exact matches for, the corresponding experimental vibrations. Figure 3a (Gd(III) benzoate monohydrate) and Figure 4b (anhydrous Ho(III) acetate) show in

graphic form the excellent agreement between the simulated and experimental IR spectra. It may be noted that, at first inspection, some of the numerical data reported for the formate and acetate models do not appear to be a good simulation of the experimental data. For example, the  $\text{COO}^- \nu_{\text{as}}$  vibration, listed at  $1546 \text{ cm}^{-1}$  for the formate model, appears as an erroneous prediction of the same vibration that occurs at  $1580 \text{ cm}^{-1}$  in the compound. This discrepancy results from the fact that numerical frequency values do not provide information about the broadness of the experimental band and Figure 3b shows that the simulated spectrum of the formate model provides a much closer match to the experimental IR spectrum than do tabulated numerical data. This emphasizes the value of graphical data when assessing the accuracy of a model structure with regard to geometry or coordination number, since reliance on numerical data alone may give misleading results.

The slight shifts of the sharp carboxylate absorptions in the simulated mid-IR spectra of the models relative to the broad absorptions of the experimental spectra is due to the inaccurate representation in the models of the carboxylate bridging present between neighboring molecules in a crystal lattice for the compounds. Since the model structures were constructed as single molecules, interactions between adjacent molecules were not computed.

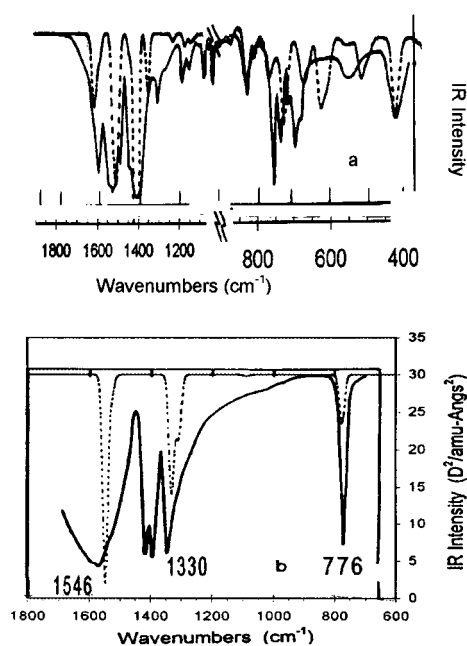
(b) The O—C—O  $\delta$  and Ln—O  $\nu$  modes for all the acetate and benzoate complexes are listed in Table 2. The normal coordinate analysis was able to distinguish coordinated water from chelate rings in that these modes vibrated at a frequency unique to each ligand. Absorptions due to vibrations within chelate rings in the acetate models and compounds<sup>18,22</sup> occurred at  $\sim 660 \text{ cm}^{-1}$  and  $265\text{--}235 \text{ cm}^{-1}$ ; the coordinated water bands occurred in two general regions: at  $560\text{--}500 \text{ cm}^{-1}$  and  $350\text{--}300 \text{ cm}^{-1}$ . Absorptions due to chelate rings in Gd(III) benzoate monohydrate<sup>21,23</sup> occurred at 680, 420, and  $174 \text{ cm}^{-1}$ ; the coordinated water band occurred at  $\sim 350 \text{ cm}^{-1}$ .

(c) The simulated mid-IR spectra of the acetates changed minimally, as expected, when the coordination number of the models was varied; in contrast, the far-IR spectra of the models changed drastically. As for the chloride models, the match of the calculated Ln—O frequencies to the experimental data allowed the successful prediction of the number

**Table 2.** Simulated Carboxylate Vibrations Compared to Experiment

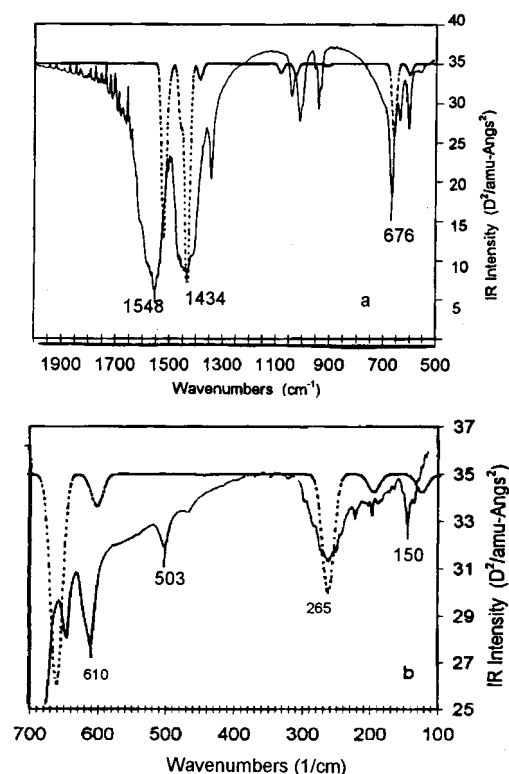
compound	C.N.	COO <sup>-</sup> $\nu_a$	COO <sup>-</sup> $\nu_s$	O—C—O $\delta$	Gd—O $\nu$	Ho—O $\nu$
<b>formate</b>						
Gd(OOCH <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	not reported	1580 br	1359	785	250 br	
<b>model</b>			<b>calculated</b>	<b>modes</b>		
Gd(OOCH <sub>3</sub> ) <sub>3</sub> anhydrous	6	1546	1330	776	248 br	
<b>acetates</b>						
Ln(OOCCH <sub>3</sub> ) <sub>3</sub> hemihydrate	not reported	1548	1434	678	259	265
Ln(OOCCH <sub>3</sub> ) <sub>3</sub> trihydrate	9	1543	1457	682	240	239
<b>models</b>			<b>calculated</b>	<b>modes</b>		
Ln(OOCCH <sub>3</sub> ) <sub>3</sub> anhydrous	6	1522	1432	660	262	266
Gd(OOCCH <sub>3</sub> ) <sub>3</sub> monohydrate	7	1530	1434	656	251	
Gd(OOCCH <sub>3</sub> ) <sub>3</sub> dihydrate	8	1542	1434	652	260	
Ln(OOCCH <sub>3</sub> ) <sub>3</sub> trihydrate	9	1548	1434	650	234	238
<b>benzoate</b>					<b>impure mode</b>	<b>Gd—O <math>\nu</math></b>
Gd(C <sub>6</sub> H <sub>5</sub> COO) <sub>3</sub> monohydrate <sup>b</sup>	not reported	1520 br	1410	680	419 <sup>c</sup>	not reported
<b>model</b>			<b>calculated</b>	<b>modes</b>		
Gd(C <sub>6</sub> H <sub>5</sub> COO) <sub>3</sub> monohydrate	7	1508	1408	680	426 <sup>c</sup>	174

<sup>a</sup> The data for this anhydrous compound comes from ref 19. <sup>b</sup> The data for this compound comes from ref 21. <sup>c</sup> The absorptions at  $\sim 420$  cm<sup>-1</sup> are a mixed mode of O—C—O bending and Gd—O stretching vibrations.<sup>21,23</sup>



**Figure 3.** Overlay of the experimental spectra (continuous lines) to the simulated spectra (dotted lines) of (a) Gd(III) benzoate monohydrate and (b) anhydrous Gd(III) formate. The experimental spectrum in (a) taken from ref 20. The experimental spectrum of La(OOCH<sub>3</sub>)<sub>3</sub> in (b) taken from ref 18.

of water molecules bound to Ln(III) in the acetate complexes. For example, the model containing three waters of hydration was the only model that produced a match between the calculated and experimental Ho—O stretching vibration at 239 cm<sup>-1</sup> in the spectrum of Ho(III) acetate trihydrate. Similarly, the Ln—O absorptions at 259 cm<sup>-1</sup> (Gd—O) and 265 cm<sup>-1</sup> (Ho—O) for the hemihydrate compounds matched the Ln—O frequencies of the anhydrous and dihydrate



**Figure 4.** (a) Overlay of the experimental spectrum of Gd(III) acetate hemihydrate to the simulated spectrum (dotted line) of anhydrous Gd(III) acetate and (b) overlay of the far-IR spectrum of Ho(III) acetate hemihydrate to the simulated spectrum (dotted line) of anhydrous Ho(III) acetate.

models. However, the dihydrate model produced prominent water absorptions at 534 and 498 cm<sup>-1</sup> that were absent in the experimental spectrum of the hemihydrate. Thus, based on the far-IR bands, the dihydrate model was rejected for



having the incorrect number of water groups for the hemihydrate complex. The absence of any water bands in the spectrum of the anhydrous model confirms that this structure best indicates the level of water present in the hemihydrate compound, which is near zero.

The exact match between of the far-IR bands for Ln(III) acetate hemihydrate and those of the anhydrous model (C.N. 6) does not imply that the Ln(III) ion in the hemihydrate complex forms only six Ln–O bonds. Due to the polymeric structure known to exist in crystalline acetates, these compounds usually exhibit a C.N. of 8 or 9.<sup>24,25</sup> In this case, the exact match of the spectra indicates only that the anhydrous model provided the correct number of water molecules coordinated to Ln(III) and does not indicate the coordination number. Because of the difficulties in constructing bridging structure in ab initio models, polymeric carboxylate compounds are not suitable to test whether the ROHF/SBKJC method can predict the coordination numbers of mononuclear complexes.

**3. Geometry.** All models of the compounds were optimized under  $C_1$  symmetry in order to evaluate the ECP method as a useful tool for predicting IR spectra in complexes of unknown symmetry. Due to the low symmetry control and/or the polymeric structure of the compounds considered, an exact prediction of the crystal geometries was not expected. However, approximate geometries were obtained and the calculated bond lengths were in good agreement with experiment. The calculated Gd–Cl bond lengths in the  $[\text{GdCl}_2 \cdot 6\text{H}_2\text{O}]^+$  model were 2.813 Å and the Gd–Cl lengths in the crystalline compound are 2.768 Å.<sup>8</sup> The calculated Gd–O bond lengths ranged from 2.42 to 2.47 Å and the crystal exhibits Gd–O lengths of 2.39–2.42 Å.<sup>8</sup>

Similar agreement was obtained for the anhydrous and hydrated acetates. In the anhydrous acetate models the calculated Ln–O bond lengths ranged from 2.33 to 2.37 Å; the experimental lengths in anhydrous Ho(III) acetate ranged from 2.24 to 2.56 Å.<sup>24</sup> In the trihydrate models, the Ln–O bonds involved in the chelate rings had lengths that ranged from 2.35 to 2.52 Å, and the Ln–O bonds due to coordinated water were 2.52–2.58 Å in length. In comparison, the bond lengths for all Eu–O distances in Eu(III) acetate trihydrate were 2.397 Å.<sup>26</sup>

## CONCLUSIONS

The ROHF/SBKJC method in GAMESS was successfully used to simulate mid- and far-IR spectra for Ho(III) and Gd(III) chlorides as well as for the formate, acetate, and benzoate complexes of these two lanthanide ions. In all cases, the computed IR spectra were in good qualitative agreement with experiment; in some cases, excellent matches were obtained. Conversion of the computed normal modes into Gaussian band shapes, through the IRSIM program, effectively demonstrated the advantage of comparing IR data in spectral rather than numerical form, when predicting C.N., type of coordination, and amount of bonded solvent for complexes with unknown structures. Absorptions arising from metal–oxygen stretching modes of chelated carboxylate groups were successfully distinguished from those due to coordinated water. The number of coordinated water molecules was accurately predicted in Ln(III) chloride hexahydrate and in the acetate compounds.

This research represents the first successful attempt to model large lanthanides complexes employing effective core potentials in ab initio calculations. Based on the IR data obtained in this work, the ROHF/SBKJC method shows promise as an effective predictive tool for the elucidation and speciation of lanthanides in complexes containing more than 10 atoms.

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