Excited state properties of Cr$^{3+}$ in Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$: A density functional study

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(Received 7 November 1995; accepted 12 February 1996)

The ground and excited state properties of the Cr$^{3+}$ ion doped into the cubic host lattices Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ have been studied using density functional theory. A new symmetry based technique was employed to calculate the energies of the multiplets $^4A_{2g}$, $^4T_{2g}$, $^2E_g$, and $^4T_{1g}$. The geometry of the CrX$_6^{3-}$ cluster was optimized in the ground and excited states. A Madelung correction was introduced to take account of the electrostatic effects of the lattice. The experimental Cr–X distance in the ground state can be reproduced to within 0.01 Å for both chloride and bromide systems. The calculated $d-d$ excitation energies are typically 2000–3000 cm$^{-1}$ too low. An energy lowering is obtained in the first $^4T_{2g}$ excited state when the octahedral symmetry of CrX$_6^{3-}$ is relaxed along the $e_g$ Jahn–Teller coordinate. The geometry corresponding to the energy minimum is in excellent agreement with the $^4T_{2g}$ geometry derived from high-resolution optical spectroscopy of Cs$_2$NaYCl$_6$:Cr$^{3+}$. It corresponds to an axially compressed and equatorially elongated CrX$_6^{3-}$ octahedron. © 1996 American Institute of Physics. [S0021-9606(96)00519-7]

I. INTRODUCTION

The properties of low-lying electronic excited states of transition metal ions in coordination compounds and as dopants in ionic lattices are of great current interest. On the chemical side this interest is mainly motivated by the photo-catalytic, photochemical, and photosensitiser properties of some coordination compounds.1 On the physical side it is driven by the potential of some transition metal ion doped systems as laser or phosphor materials.2 The Cr$^{3+}$ ion plays a particularly important role, because it exhibits luminescence in the near infrared (NIR) part of the spectrum, and coordination compounds with a great variety of ligands are photochemically active. Cr$^{3+}$ has a very strong preference for octahedral coordination, and depending on the nature of the coordinating ligand the first excited state is either $^2E_g$ or $^4T_{2g}$. Ruby, i.e., Cr$^{3+}$ in Al$_2$O$_3$, is the prototype example of a strong-field case with a $^2E_g$ first excited state exhibiting a long lived sharp-line $^2E_g$→$^4A_{2g}$ luminescence around 700 nm. In the title compounds we have a weak-field situation with a $^4T_{2g}$ first excited state and, consequently, a shorter lived broad-band luminescence in the NIR. A thorough exploration of this low-field situation is the subject of the present paper.

There is an abundant literature on Cr$^{3+}$ photochemistry.1–3 In the large majority of Cr$^{3+}$ coordination complexes, the first excited state is $^2E_g$, but the $^4T_{2g}$ state can become thermally accessible at room temperature. It is established that for some cases the $^4T_{2g}$ state plays an important part in the photochemical mechanisms. But it is not clear whether this is true for all complexes, and the detailed mechanisms of photosubstitution are far from being understood. A Jahn–Teller distortion of the $^4T_{2g}$ state in Cr(NH$_3$)$_6^{3+}$ has been proposed as a possible factor for subsequent substitution steps.4

Most Cr$^{3+}$ doped halide lattices exhibit broad-band luminescence in the NIR. In fluorides the Cr$^{3+}$ ion is close to the crossover point between the $^2E_g$ and $^4T_{2g}$ first excited states, but in all chlorides and bromides the emitting state is $^4T_{2g}$.5 Broad-band $^4T_{2g}$ emission can even be obtained in some oxo environments at room temperature. The most prominent example is Cr$^{3+}$ doped alexandrite, an established laser material with a tuning range from about 740 nm to 820 nm.6 Some Cr$^{3+}$ doped glasses and glass ceramics exhibit emissions extending from about 700 nm out to about 1 mm.7 In recent years some new materials with great promise for laser applications have been developed. Cr$^{3+}$ doped LiCaAlF$_6$(LiC$\alpha$F) and LiSrAlF$_6$(Li$\alpha$SAF) are broad-band emitters with favorable crystal and excited-state properties. Li$\alpha$SAF:Cr$^{3+}$ has a laser tuning range from 770 nm to 920 nm at room temperature.8 An advantage of halides as compared to oxides lies in their lower phonon energies. Multiphonon relaxation processes, which compete with radiative processes and are thus detrimental for laser action particularly in the IR, are less efficient.

Numerous detailed optical spectroscopic and theoretical studies of the radiative and nonradiative $^4T_{2g}$→$^4A_{2g}$ processes of Cr$^{3+}$ in a variety of crystal lattices have been reported in the literature. We have chosen the elpasolite host lattices Cs$_2$NaYCl$_6$, Cs$_2$NaInCl$_6$, and Cs$_2$NaYBr$_6$ because they exhibit a great deal of fine structure in their low-
temperature luminescence spectra. Thanks to the exactly octahedral point symmetry, the analysis of the fine structure can be pushed to a point at which the excited states are thoroughly characterized with respect to energy, structure and dynamics. The $^1T_2g$ excited state couples to both the $a_{1g}$ and, in a dynamical Jahn–Teller effect, the $e_g$ vibration of the CrX$_6^{3-}$ octahedron. The result is a distorted geometry of the excited state with an axial compression and an equatorial elongation of the octahedron. From the thermal quenching behavior it was concluded that the relevant multiphonon relaxation processes involve the same $a_{1g}$ and $e_g$ modes which are responsible for the excited state distortion.

We have performed recently a theoretical investigation of the excited state properties and the Jahn–Teller effect in [CrX$_6$]$^{3-}$ (X=Cl, Br) by using density functional theory (DFT). In addition to the $^4A_2$ ground state, the properties of the $^2E$, $^4T_2$, and $^4T_1$ excited states have been calculated by taking into account multiplet structure effects. The emphasis was placed on the influence of metal-ligand distance on the multiplet energies and on the Jahn–Teller distortion exhibited by the $^4T_2$ excited state. It was found that the latter state moves to a stable geometry when the axial bond is compressed and the equatorial one elongated, in agreement with the experimental observations.

The purpose of the present study is to calculate the ground and excited state properties of Cr$^{3+}$ in the cubic chloride and bromide elpasolite lattices. In particular, we are interested to enlarge the previous investigation by including a Madelung potential due to the effect of the lattice. This is a severe and crucial test of the theoretical method. Indeed, if the Jahn–Teller distortion cannot be reproduced, the method does not hold much promise to ever predict the relevant photophysical and photochemical properties of transition metal ions hosted in ionic lattices. The density functional technique used in the present work has been also successfully applied before to compute excited state properties of the rhenocene complex.

II. COMPUTATIONAL METHODS

A. Density functional calculations

The linear combination of Gaussian-type orbital-model core potential-density functional (LCGTO-MCP-DF) method and its corresponding deMon program package have been used. A slight modification of this program code has been made in the calculation of three-center integrals to take account of the Madelung potential (MAP). The Vosko–Wilk–Nusair (VWN) local exchange-correlation potential has been used in this study. In addition, in all cases, the influence of nonlocal gradient corrections as suggested by Becke for exchange and Perdew for correlation functionals (BP) has also been investigated. All the core and valence electrons were explicitly taken into account.

The one-electron (orbital) basis set used in the calculations has been optimized for LCGTO-DF calculations by Godbout and Andzelm. The Cr, Cl, and Br basis sets are of double zeta plus polarization quality, the contraction patterns being Cr (63321/5211/41), Cl (7321/621/1), Br (63321/5321/41), which leads in the usual six-component $d$-type Gaussian functions to a basis set of dimensions 143 for [CrCl$_6$]$^{3-}$ and 203 for [CrBr$_6$]$^{3-}$. The auxiliary basis sets required by the LCGTO-DF model to fit the electron density and the exchange-correlation potential have been chosen as Cr (5,5,5,5), Cl (5,4,5,4), and Br (5,5,5,5).

B. Multiplet structure

The calculation of the multiplet structure in DFT has been discussed recently by Daul. According to these results, it is possible to replace the energy of a single determinant by the corresponding statistical energy as obtained in DFT. The energy of a multiplet arising from a given configuration being a weighted sum of single-determinantal energies, it is thus possible to obtain the multiplet splittings to first order.

Following the same methodology, we used symmetry based arguments to rationalize the relation between the multiplet splittings and single-determinantal energies. It is thus possible to obtain the multiplet splittings to first order. The three lowest terms of the Cr(III) free ion 3d$^3$ configuration, i.e., $^4F$, $^4P$, and $^2G$, are reduced in an octahedral environment as follows:

- $^4F \rightarrow ^4A_{2g} + ^4T_{2g} + ^4T_{1g}$
- $^4P \rightarrow ^4T_{1g}$
- $^2G \rightarrow ^2E_g + ^2T_{1g} + ^2T_{2g} + ^2A_{1g}$

One purpose of our work was to explore the potential energy surfaces of the low-lying excited multiplets as a function of metal-ligand bond length $d$(Cr–L) and to determine their minima. The following multiplets were considered in our calculation: $|t_2^2 A_2^2 |$, $|t_2^2 2E |$, $|e t_2^2 4T_2 |$, and $|e t_2^2 4T_4 |$. Their energies can be obtained as shown below from the energies of the following DFT single determinants:

- $E(^4A_2) = E(|\xi^+ \eta^+ \xi^+|)$
- $E(^4T_2) = E(|u^+ \xi^+ \eta^+|)$
- $E(^4T_4) = E(|v^+ \xi^+ \eta^+|)$

$E(^2E) = 1.5E(|\xi^+ \eta^+ \xi^-|) - 0.5E(|\xi^+ \eta^+ \xi^+|)$

where $u$ and $v$ are the components of $e_g$ ($d_2^2$ and $d_{z^2}-y^2$, resp.) and $\xi$, $\eta$, and $\zeta$ the components of $t_{2g}$ ($d_{yz}$, $d_{xz}$, and $d_{xy}$, resp.).

Since the deMon program does not use symmetry adapted basis functions, a small tetragonal elongation of 0.008 Å is arbitrarily used to induce a tiny splitting in order
to identify the components of $e_g$ and $t_{2g}$. This distortion has no significant consequence on the calculation. 10

C. Madelung potential

1. Method

It is known that, in ionic crystals, the Coulombic interaction between a given cluster and the surrounding lattice may be described using a so-called Madelung potential. In order to evaluate the importance of this term on both the potential energy surface and the electronic structure of the reference cluster $\text{CrX}_6^{3-}$, two series of calculations were performed. In the first one, the external potential $V_{\text{ext}}(\mathbf{r})$ was expressed in terms of the usual Kohn–Sham Hamiltonian,

$$V_{\text{ext}}(\mathbf{r}) = \sum_{m=1}^{M_n} \frac{Z_m}{|\mathbf{R}_m - \mathbf{r}|},$$

where the summation runs over the $M_n$ nuclei of the first neighboring shell atoms.

In the second one, a Coulombic contribution, $V_{\text{mad}}(\mathbf{r})$, arising from the Madelung potential was added as follows:

$$V_{\text{eff}}(\mathbf{r}) = \sum_{m=1}^{M_n} \frac{Z_m}{|\mathbf{R}_m - \mathbf{r}|} + \sum_{L=1}^{L_{\text{max}}} \frac{q_L}{|\mathbf{R}_L - \mathbf{r}|},$$

where the second summation runs over a selected set of point charges $q_L$ with positions $\mathbf{R}_L$. Obviously, in the present case, the condition of charge neutrality requires that

$$\sum_{L=1}^{L_{\text{max}}} q_L = +3.$$  

The problem of finding adequate charges $q_L$ and positions $\mathbf{R}_L$ was approached in two different ways: (i) ionic charges are located at the positions of successive neighboring shell atoms of the elpasolite lattice; (ii) a limited set of $(q_L;R_L)$ values is determined by least-squares fitting to Madelung potential values due to the surrounding lattice at selected points of the cluster. The first procedure was adopted in spite of its slow convergence, see Fig. 1(a). The fitting was indeed found to be too inaccurate for a proper description of the potential energy surface of the cluster, as it is important to
perform an adequate modelling of the Madelung potential throughout the whole cluster volume [Fig. 1(b)] and not in highly symmetrical directions only.

2. Point charges

With this type of model for the Madelung potential there is the problem of which charges to assign to the lattice atoms. The atomic charges can possibly be derived from calculations based either on a periodic treatment of the crystal or on a cluster model of the surrounding. Both methods may lead to a reasonable estimation of the atomic charges, but it is well known that population analysis methods are somewhat arbitrary. This explain why we have decided to use formal charges of +1 for Cs and Na, +3 for Y and −1 for Cl and Br for $q_L$ values of Eq. (2). Indeed, elpasolites are undoubtedly crystals with an high ionic character and, furthermore, the ionic model leads to the largest contribution of the crystal field. However, a second problem arises due to the size of the cluster, i.e., the number of shells of neighboring atoms, to be chosen to calculate the Madelung potential. Therefore, we have investigated first the rate of convergence of the MAP calculated at the Cr$^{3+}$ site as a function of the number of point charges $q_{L}$ used [Fig. 1(a)]. It is seen in this figure that the MAP exhibits variations of nearly 0.1 a.u., even for a very large number of point charges (superior to 30 000 $q_{L}$). In order to evaluate the effect of these oscillations on the potential energy surfaces, some structural and spectroscopic properties have been calculated for the $^4A_2$ and the $^4T_2$ states using two sets of point charges, namely 8336 and 9592. A difference of 0.08 a.u. has been thus obtained for the MAP at the Cr$^{3+}$ site. The potential energy curves calculated as a function of the Cr–Cl distance for these two different MAPs are displayed in Fig. 1(c) (ground-state) and Fig. 1(d) (first excited-state). As the number of point charges increases, the optimum bondlengths shorten by 0.001 Å and 0.0015 Å for the $^4A_2$ and the $^4T_2$ states, respectively. This indicates that the influence of the number of point charges used in the MAP is very small, provided a sufficiently large set of such charges is employed. Therefore, all the calculations reported here have been performed with a MAP calculated using 9592 $q_{L}$.

D. Frequencies

Vibrational frequencies of CrX$_6^{3-}$ normal modes were determined approximately by calculating the total energy $E$ as a function of small $a_{1g}$ and $e_{g}$ symmetry-adapted displacements, as shown in the Fig. 2, of the six nearest halogen neighbors of the chromium impurity. The potential energy curves obtained were fitted by using the harmonic approximation. The normal modes $Q_{k}$ are appropriate combinations of the mass-weighted coordinates expressed as follows:

$$Q_{a}(a_{1g}) = N_{a_{1g}}(x_1 - x_4 + y_2 - y_5 + z_3 - z_6),$$

$$Q_{p}(e_{g}) = N_{e_{g}1}(2z_3 - 2z_6 - x_1 + x_4 - y_2 + y_5),$$

$$Q_{q}(e_{g}) = N_{e_{g}2}(x_1 - x_4 - y_2 + y_5),$$

where $N_{a_{1g}}, N_{e_{g}1}, N_{e_{g}2}$ are mass dependent normalization factors and $x_L, y_L, z_L$ the Cartesian coordinates of ligand $L$ (Fig. 2). Frequencies $\omega$ are finally calculated as

$$\omega = \sqrt{\frac{k}{\mu_L}},$$

where $k$ and $\mu_L$ are the force constant and the reduced mass, respectively.

III. RESULTS AND DISCUSSION

A. Ground state geometry and force constants

The main purpose of the present paper is to report on the influence of introducing a Madelung correction to the results discussed in the previous article.$^{10}$ To this end, we have mostly used the BP exchange-correlation potential which was found in the previous paper to be the most adequate. Figures 3(a) and 3(b) show the ground-state potential energy curves thus obtained for both the chloride and the bromide. The minima of the curves are shifted towards shorter Cr–X distances when the Madelung potential term is included, but it has only a small effect on the Cr–X equilibrium distance. For both the chloride and the bromide, it leads indeed to a shortening of the Cr–X distance by 0.02–0.03 Å. Comparisons between BP and BP-MAP results obtained for the first excited state in the octahedral approximation are presented in Figs. 4(a) and 4(b). The differences are similar to those observed for the ground state.

The effect of the Madelung potential is to shorten the metal-ligand bond distances$^{10}$ whatever local$^{16}$ or nonlocal functionals are used.$^{17-19}$ The corresponding force acting on the ligands, derived from the gradient of the Madelung potential along the Cr–X bond at the X position, as displayed
in Fig. 1(b), is oriented towards the metal and tends to shorten the bond length. Furthermore, this force is practically independent on the level of accuracy of the MAP potential. Calculations performed on the $^{3}A_2^g$ ground state show that a reduced set of 420 point charges, instead of 9592, leads to a proper description of the effect of the lattice on the M–L distance; no calculation with such a reduced set has been performed for the geometry of the excited states $^4E_g$, $^4T_1^g$, and $^4T_2^g$. However, the information presented in Fig. 1(b) allows us to suggest that the same trend may be expected as that of the $^{3}A_2^g$ ground state.

Comparing the calculated Cr–X distances with the experimental ones, we have to consider that the latter ones have not been determined in these doped lattices. The last column of Tables I and II, therefore, contains two values, one estimated for pure Cs$_2$NaCrX$_6$ and one determined for the host lattice $^{22}$Cs$_2$NaYX$_6$. The discrepancy is due to a difference of roughly 0.3 Å in the ionic radii of Cr$^{3+}$ and Y$^{3+}$. The Cr$^{3+}$ ion is therefore located in a hole within the Cs$_2$NaYX$_6$ elpasolite host lattice which is too large, and the exact Cr–X distance is not known. The fact that the spectroscopic properties of Cs$_2$NaInCl$_6$:Cr$^{3+}$ are very similar to Cs$_2$NaYCl$_6$:Cr$^{3+}$ indicates that the actual Cr–X distance is much closer to that in Cs$_2$NaCrX$_6$ than to the Y–X distance in Cs$_2$NaYX$_6$. We conclude therefore that our calculated Cr–X distances are too large by 0.1 Å at most, which may be considered as a good agreement for this type of calculation. The Madelung correction exhibits the right trend, but its magnitude is insufficient to bring the values down to those of pure Cs$_2$NaCrX$_6$. In a recent $ab$ initio Hartree–Fock calculation, no distinction was made between the $M^{3+}–X^-$ distance of the host lattice and the local CrX$_6^{3—}$ cluster. $^{25}$ In view of the large difference in the ionic radii we think this effect should be taken into account. A rather large Cr–Cl distance of 2.58 Å was reported in Ref. 25.

B. Electronic excitation energies

High-resolution absorption, MCD and luminescence spectra have been reported for Cs$_2$NaYCl$_6$:Cr$^{3+}$. $^{5,24}$ Accu-
rate values of the excited state energies are therefore known and included in Table I. In particular, the region of $^4A_2 \rightarrow ^4T_2$ electronic origins was investigated in detail, and the energies of all the four spin–orbit components of $^4T_2$ were determined. The total splitting of $^4T_2$ was found to be reduced from about 105 cm$^{-1}$ to 33 cm$^{-1}$ as a result of a Ham effect. This Ham quenching was one of the experimental observables which were used for a derivation of the Jahn–Teller energy and the Jahn–Teller distortion, see also Sec. IV B. In the bromide host lattice the Cr$^{3+}$ spectra are

<table>
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<tr>
<th>$^4A_2 \rightarrow ^4T_2$</th>
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<td>12 550</td>
<td>9 760</td>
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<tr>
<td>11 030</td>
<td>8 382</td>
<td>8 010</td>
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<tr>
<td>1 520</td>
<td>1 378</td>
<td>1 798</td>
<td>1 800</td>
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Stokes shift

$^4T_2 \rightarrow ^4A_2$

$\Delta [Cr–Cl(x,y)]$ $\Delta [Cr–Cl(z)]$

-0.07 $\rightarrow$ -0.05 $\rightarrow$ -0.03$^d$

$A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

Vib. Freq. $^A_2$

$\alpha_g$ $\epsilon_g$

- $^4A_2$

$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

Vib. Freq. $^A_2$

$\alpha_g$ $\epsilon_g$

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$^4A_2 \rightarrow ^2E$

max. abs.

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max. abs.

Jahn–Teller energy

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$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

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max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

Vib. Freq. $^A_2$

$\alpha_g$ $\epsilon_g$

- $^4A_2$

$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

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$\alpha_g$ $\epsilon_g$

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$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

Vib. Freq. $^A_2$

$\alpha_g$ $\epsilon_g$

- $^4A_2$

$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$

max. abs.

Jahn–Teller energy

Vib. Freq. $^A_2$

$\alpha_g$ $\epsilon_g$

- $^4A_2$

$^4A_2 \rightarrow ^2E$

max. abs.

$^4A_2 \rightarrow ^2T_1$
C. Excited state distortions

The title compounds are among the very few transition metal ion systems for which enough spectroscopic data exist to derive accurate information about geometrical distortions in an excited ligand field state. A particular attraction of the present compounds lies in the fact that they belong to the low-field family of \(\text{Cr}^{3+}\) systems and the emitting \(4T_{2g}\) state is susceptible to a Jahn–Teller effect. Since \(\text{Cr}^{3+}\), substituting for \(\text{Y}^{3+}\), occupies an exactly octahedral site in these elpasolite lattices, the consequences of the Jahn–Teller coupling become observable and analyzable. The highly resolved luminescence spectrum of \(\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}\) at cryogenic temperatures formed the basis of the experimental analysis, the distortions in the bromide were obtained by analogy. There are two independent but very consistent manifestations of a Jahn–Teller coupling of the \(4T_{2g}\) state to the \(e_g\) vibration of the \(\text{CrX}_6^{2-}\) cluster; one is the observation of a progression in this \(e_g\) vibration in the \(4T_{2g} \rightarrow 4A_{2g}\) luminescence spectrum at 7 K and the other one is the partial quenching of the \(4T_{2g}\) spin–orbit splitting through a Ham–effect mentioned in Sec. IV B. A Jahn–Teller energy of 310 cm\(^{-1}\) and an axially compressed and equatorially elongated geometry of the \(\text{CrCl}_6^{2-}\) cluster with \(δ[\text{Cr–Cl(\text{xy})}]=0.10\) Å and \(δ[\text{Cr–Cl(\text{yz})}]=0.03\) Å was obtained from a detailed analysis of the Huang–Rhys factors for the \(a_{1g}\) and \(e_g\) distortions.

Let us first discuss Fig. 5, which shows the disposition of the potentials of the first excited states with respect to the ground state in the octahedral approximation. For both the chloride and the bromide systems the minima of \(2E_g\) and \(4A_{2g}\) occur at approximately the same \(\text{Cr}–\text{X}\) distance. This is a reflection of the fact that in first order the \(4A_{2g} \rightarrow 2E_g\) excitation simply corresponds to a spin-flip within the \(t_{2g}\)\(^3\) electron configuration. Sharp absorption lines corresponding to a Huang–Rhys factor close to zero are the experimental...
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FIG. 6. Contour levels of the $^4T_{2g}$ potential energy surface calculated as a function of both Cr–X(x, y) and Cr–X(z) bond distances for the chloride (a) and bromide (b) including both the Jahn–Teller distortion and the Madelung correction. The origin of both axes corresponds to the calculated ground-state geometry of Fig. 3. The asterisks indicate the experimental excited state geometry. Energy in cm$^{-1}$.

Along the $e_g$ coordinate which leads to an axial compression and an equatorial elongation of the octahedron. The geometry corresponding to the energy minimum is in almost perfect agreement with the experimentally derived value for both the chloride and the bromide. Even if we consider this exact agreement as fortuitous, this result is very gratifying. We conclude that DFT calculations of the type reported here are able to reproduce geometries of excited $d$–$d$ states in transition metal ion complexes or crystals. In particular, the consequences of a Jahn–Teller coupling in the excited state, i.e., an energy gain by lowering the octahedral symmetry, can be obtained very accurately in such a calculation. The DFT technique should therefore have some predictive value. This is very important because there are only very few examples of transition metal ions in complexes and crystals, in which the first excited states have been studied by high-resolution spectroscopy in as much detail as the title compounds. It is unusual that a spin-allowed $d$–$d$ band exhibits such fine structure as the $^4T_{2g}$–$^4A_{2g}$ luminescence in Cs$_2$NaYCl$_6$·Cr$^{3+}$. Usually such bands are featureless, and for many photochemically relevant complexes there is no experimental information about excited state distortions. We feel that the DFT technique presented here holds some promise to obtain an estimate of such distortions. This will be of high relevance to photochemistry and photophysics. In a similar way, the laser materials oriented research could profit from the possibilities of predicting excited state distortions. On the one hand, the spectral band widths and shapes are determined by such distortions. On the other hand, there is good evidence, at least in the case of the title compounds, that the modes which distort the excited state are the active accepting modes in multiphonon relaxation processes. Such nonradiative processes are detrimental for laser action and thus highly significant for the search and development of new materials.

ACKNOWLEDGMENTS

The authors are grateful to Professor D. R. Salahub and to Professor E. J. Baerends for providing copies of their DFT programs and for fruitful discussions. Financial support by the Swiss National Science Foundation and the Federal Office for Education and Science, acting as Swiss COST Office, is gratefully acknowledged.