Chapter 6

Enhancement of IR and VCD intensities due to charge transfer

6.1 Introduction

In this chapter we investigate the enhancement of the VCD intensities of the N–H stretching modes of the tris(ethylenediaminato)cobalt(III) transition metal complex induced by the association of the chloride ions.

The tris(ethylenediaminato)cobalt(III) complex, [Co(en)_3]^{3+}, is a prototype chiral transition metal complex. Over the years, its optical activity has been extensively studied using spectroscopic techniques like anomalous X-ray [94, 95], electronic circular dichroism [96–100], NMR [101–103], and VCD [55, 84]. The configurations of the [Co(en)_3]^{3+} complex can be classified as follows. A tris(bidentate) complex can exist in a right-handed (∆) and left-handed (Λ) form (see Fig. 6.1), using the pseudo-threefold axis of the octahedron as the defining axis.

The ∆ and Λ form can exist in various conformations dependent on the conformations of the individual bidentate ligands. An ethylenediamine ligand coordinates to the metal center with the two N lone pairs, forming a puckered five-membered ring. When viewing the metal through the midpoint of the C–C bond, there are two possible conformations for the N–C–C–N bonds (see Fig. 6.2): either the C atom to the left is down and the C atom to the right is up (∆ configuration), or the C atom to the left is up and the C atom to the right is down (δ configuration).

Both the Λ and ∆ configurations of [Co(en)_3]^{3+} can therefore exist in four different conformations labeled as δδδ, δδλ, δλλ and λλλ. In the Λ enantiomer the δ en ligand has the C–C bond nearly parallel to a C_3 axis, while the λ en
form has the C–C bond oblique to the \( C_3 \) axis [104] (see Fig. 6.3 left panel). In the \( \Delta \) enantiomer the situation is reversed, the C–C bond of the \( \lambda \) en ligand is nearly parallel to a \( C_3 \) axis, while the C–C bond of the \( \lambda \) en ligand is oblique to the \( C_3 \) axis (see Fig. 6.3 right panel).

From now on we will restrict ourselves to the \( \Lambda \) configurations, and note that *mutatis mutandis* a similar situation will hold for the enantiomeric \( \Delta \) forms. Now in the \( \Lambda - \delta \delta \delta \) conformation one can distinguish two sets of three N atoms. The first set forms a triangle around the positive \( z \) axis, whereas the second set forms a triangle around the negative \( z \) axis (the \( z \) axis is chosen along the \( C_3 \) axis). An important point for the study presented in this chapter is the orientation of the two N–H bonds at each N atom. As can be seen in Fig. 6.4 (also in Fig. 6.5) one N–H bond (the “axial” one) is practically parallel to the \( z \) axis, while the other N–H bond (the “equatorial” one) is almost perpendicular to the first one and to the \( z \) axis.
Figure 6.3: Schematic representation showing the orientation of the C–C bond with respect to the $C_3$ symmetry axis in the $\lambda$ and $\delta$ en-rings coordinated to the metal center for the $\Lambda$ (left panel) and $\Delta$ (right panel) configurations.

Figure 6.4: Schematic representation showing the orientation of the N–H$_{\text{axial}}$ bonds with respect to the $C_3$ symmetry axis in a $\delta$ en-ring coordinated to the metal center for the $\Lambda$ configuration.
A series of experimental, and combined experimental and computational VCD studies by Nafie et al. [55, 84] have shown that in the presence of excess chloride ions a specific conformation of Λ [Co(en)₃]³⁺ complex is stabilized by chloride ion association. This is the Λ − δδδ conformer. When two associated chloride anions are located at the positive and negative z axis, which as already mentioned, is also the C₃ axis, the axial N–H bonds form donor-acceptor bonds with the Cl⁻ (as the donor) by virtue of the relatively low-lying σ⁺ of the N–H bond. Three of the six N–H···Cl⁻ donor-acceptor bonds are pointing in the positive z direction, while the other three N–H···Cl⁻ bonds are pointing approximatively in the negative z direction (see Fig 6.5 right panel).

Here we investigate more closely the most favorable conformer as identified in reference [55], the δδδ conformer of Λ − [Co(en)₃]³⁺ ··· 2Cl⁻, Λ − δδδ ··· 2Cl⁻ for short. Our interest is focused on the enhancement of the IR/VCD intensities of the N–H stretching modes that involve displacements of the protons towards the associated chloride ions (N→H···Cl stretching modes). The association of the chloride ions induces a spectacular increase in the IR and VCD intensities of the N→H···Cl stretching modes, and a large redshift of the normal mode frequencies. In vibrational absorption spectroscopy, the effects described above are well known and documented [79, 80], their presence in IR spectra being long used as experimental evidence for intra- and inter-molecular hydrogen bond formation (the effects are more pronounced in the latter). In VCD spectroscopy on the other hand, the phenomenon has been little investigated. In chapter 4 using the benzoyl-benzoic acid – NH₃ complex (BBA–NH₃) as the test molecule, we have shown that the same mechanism is responsible for the enhancement of both IR and VCD intensities. However, since the VCD intensities are determined also by the cosine of the angle, ξ, between the electric and magnetic dipole transition moment, which often is close to zero since ξ is often very close to 90°, we asked the question whether the enhancement of the VCD intensities could be seen experimentally.

To the best of our knowledge the only published experimental evidence of VCD intensities enhanced by the mechanism described above are the VCD spectra of [Co(en)₃]³⁺ for the N–H/C–H stretching region measured with excess chloride ions presented by Nafie et al. in references [55, 84]. Since the origin of the enhancement was not addressed in the above mentioned studies, and since for this system (unlike for BBA–NH₃) the results of the analysis presented in chapter 4 can be directly compared to experimental data, in this chapter we analyze in detail the various contributions of the electric and magnetic dipole transition moments of the N→H···Cl modes. The aim being a better understanding of the mechanism responsible for the enhancement of the VCD intensities.
The BBA–NH$_3$ complex studied in chapter 4 had a single mode that exhibited an enhancement of its IR and VCD intensities upon complexation. It was an O–H···N stretching mode that involved the displacement of a single proton. The Λ−δδδ · · · 2Cl$^−$ complex on the other hand, has six N➔H · · · Cl stretching modes. Five of them exhibit an enhancement of the IR and VCD intensities, each of these modes involving displacements of six protons. As will be shown, the study of the more complicated Λ−δδδ · · · 2Cl$^−$ complex will reveal more aspects that play a role in the enhancement and therefore provide more insight into the enhancement mechanism.

Finally, we note that besides the calculations in reference [55], theoretical calculations of the VCD intensities enhanced upon hydrogen bonding were also reported by Sadlej et al. [70].

6.2 Theory

The IR intensity for the fundamental transition (|0⟩ → |1⟩) of the $i^{th}$ vibrational mode are given by the dipole strength ($D$) [13]:

$$D(i) = |E_{01}^i(i)|^2$$  (6.1)

As shown in chapter 2 the VCD intensity for the |0⟩ → |1⟩ of the $i^{th}$ is given by rotational strength ($R$):

$$R(i) = E_{01}(i) \cdot \text{Im}[\tilde{M}_{10}(i)]$$  (6.2)

In Eqs. (6.1) and (6.2), $E_{01}(i)$ and $M_{10}(i)$ are the electric and magnetic dipole transition moments associated with the first vibrational transition (|0⟩ → |1⟩) of the $i^{th}$ normal mode.

Within the harmonic approximation the transition dipole moments $E_{01}(i)$ and $M_{10}(i)$ can be written as a sum of atomic contributions (see chapter 2 section 2.2.5):

$$E_{01}(i) = \sum_\lambda \tilde{E}^\lambda_{01}(i), \quad M_{10}(i) = \sum_\lambda \tilde{M}^\lambda_{10}(i)$$  (6.3)

where the Cartesian components of $E_{01}$ and $M_{10}$ are defined in Eqs (2.145) and (2.146), respectively.

Further, since the APTs and the AATs have electronic and nuclear contributions, Eqs (2.147) and (2.148), the electric and magnetic dipole transition moments can be further decomposed into total electronic (el) and total nuclear (nuc) contributions:

$$E_{01}(i) = E_{01}^{el}(i) + E_{01}^{nuc}(i), \quad M_{01}(i) = M_{01}^{el}(i) + M_{01}^{nuc}(i)$$  (6.4)
Finally, as shown in chapter 3 the electronic contributions \( E_{\alpha\beta}^\lambda \) and \( I_{\alpha\beta}^\lambda \) of the APTs and AATs, respectively, can be decomposed in contributions from the occupied molecular orbitals (MO):

\[
E_{\alpha\beta}^\lambda = \sum_{j_{\text{occ}}} E_{\alpha\beta}^\lambda (j_{\text{occ}}), \quad I_{\alpha\beta}^\lambda = \sum_{j_{\text{occ}}} I_{\alpha\beta}^\lambda (j_{\text{occ}}) \tag{6.5}
\]

The MO contributions \( I_{\alpha\beta}^\lambda (j_{\text{occ}}) \) and \( E_{\alpha\beta}^\lambda (j_{\text{occ}}) \) are given by Eqs (3.10) and (3.13), respectively.

### 6.3 Computational Details

As in the previous chapters, all calculations (geometry optimization and IR/VCD calculations) were performed using the ADF program package \cite{24–26}. The BP86 and OLYP functionals and the TZP basis set were used in all the calculations. The geometries have been optimized separately for each choice of functional using the optimized described in reference \cite{44}. Very tight convergence criteria have been applied for the geometry optimization (\(10^{-6}\) Hartree for the energy and \(10^{-4}\) Hartree/Ångstrom for the gradients).

The IR and VCD spectra obtained with BP86 and OLYP were very similar. However, since the frequencies of the N\(\rightarrow\)H\(\cdots\)Cl stretching modes calculated using OLYP were closer to the experimental ones than the BP86 ones, only the OLYP results will be considered. The analysis of the normal modes and of the various contributions of the electric and magnetic transition dipole moments was done using the ToolsVCD program. ToolsVCD requires data saved during an ADF IR/VCD calculation.

For a direct comparison to experiment the calculated dipole and rotational strengths have been transformed to molar absorptivity (\(\epsilon\)) and differential molar absorptivity (\(\Delta\epsilon\)), respectively, using the following formulas \cite{16, 50}:

\[
\epsilon(\nu) = \frac{8\pi^2 N_A}{3 \cdot 2.303hc} \nu D_i(\nu) \tag{6.6}
\]

\[
\Delta\epsilon(\nu) = \epsilon_L(\nu) - \epsilon_R(\nu) = \frac{32\pi^3 N_A}{3 \cdot 2.303hc} \nu R_i(\nu) \tag{6.7}
\]

where \(N_A\) is Avogadro’s number, \(h\) is Planck constant, \(c\) is the speed of light in vacuum, and \(D_i(\nu)\) and \(R_i(\nu)\) are the dipole and rotational strengths associated to the \(i\) normal mode, \(\nu\) is the frequency of the normal mode \(i\), and \(\epsilon_L(\nu)\) and \(\epsilon_R(\nu)\) are the molar absorptivities for left and right circularly polarized light.

The VCD spectra were simulated by representing the peaks as Lorentzian bands \cite{50}. A half-width of 30 cm\(^{-1}\) was used for the associated NH-stretching
6.4 Results and Discussions

The Λ − δδδ molecule and the Λ − δδδ · · · 2Cl− complex (with the two Cl− ions situated on the C3 axis) are depicted in Fig. 6.5. In the panel to the left the complex is oriented in the standard way, with one N–Co–N axis as (vertical) z-axis. One is looking down the C3 axis and the three N–Haxial bonds pointing approximately towards the observer are clearly visible. In the panel to the right the C3 axis is taken as vertical axis, which shows the orientation of the C-C bonds approximately along this same direction, and the favorable position of the Cl− ions for interaction with the three N–Haxial bonds pointing to each of them.

Table 6.1 gives the experimental and calculated frequencies, and the IR and VCD intensities of the N-H stretching modes. The experimental data are taken

Figure 6.5: The OLYP/TZP optimized structures of Λ − δδδ and Λ − δδδ · · · 2Cl−. Left panel: Λ − δδδ viewed along the C3 axis. Right panel: Λ − δδδ · · · 2Cl− viewed along the C2 axis.
Table 6.1: Experimental and calculated frequencies, IR and VCD intensities of the N–H stretching modes of $\Lambda^{-}\left[\text{Co(en)}_3\right]^{3+}$. A) Experimental data taken from [55, 84]: $\Lambda^{-}\left[\text{Co(en)}_3\right]^{3+} 0.10$ M in $\text{D}_2\text{O}$ (upper panel), and $\Lambda^{-}\left[\text{Co(en)}_3\right]^{3+} 0.060$ M with excess Cl$^-$ (0.6 M LiCl) in DMSO-$d_6$ (lower panel). B) OLYP/TZP calculation for the $\Lambda^{-}\delta\delta\delta$ molecule (upper panel) and for the $\Lambda^{-}\delta\delta\delta\cdots{2}\text{Cl}^-$ complex (lower panel). The calculated frequencies were scaled by 1.0766 (N$\leftrightarrow$H$\cdots$Cl stretching) and by 0.9643 (free N–H stretching). Units: Freq.(1/cm) and $\epsilon_{\text{max}}$ (10$^3$ cm$^2$/mol).

<table>
<thead>
<tr>
<th>Sym.</th>
<th>Exp. Freq.</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$10^3\Delta\epsilon_{\text{max}}$</th>
<th>Th. Freq.</th>
<th>$\epsilon_{\text{max}}$</th>
<th>$10^3\Delta\epsilon_{\text{max}}$</th>
<th>Sym.</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>3041</td>
<td>792</td>
<td>+200</td>
<td>3015.2</td>
<td>41.1</td>
<td>$-244.1$</td>
<td>$E$</td>
<td>180$^\circ$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>3125</td>
<td>1098</td>
<td>$-89$</td>
<td>3019.4</td>
<td>129.4</td>
<td>$+296.9$</td>
<td>$2E$</td>
<td>0$^\circ$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3148.6</td>
<td>1973.8</td>
<td>$-67.8$</td>
<td>$A_2$</td>
<td>180$^\circ$</td>
</tr>
</tbody>
</table>

In Section A of Table 6.1 (left panel) the experimental measurements for $\Lambda^{-}\left[\text{Co(en)}_3\right]^{3+} 0.10$ M with 1 M DCl in $\text{D}_2\text{O}$ are compared with those for $\Lambda^{-}\left[\text{Co(en)}_3\right]^{3+} 0.060$ M with 0.6 M LiCl in DMSO-$d_6$ (a 10-fold excess of chloride anion per complex). We note that out of the 12 N-H modes there are two (with $A_1$ symmetry) that have zero intensity. Furthermore, in the experiment some modes have such low intensity that they are not observed (e.g. the $E$ modes in the IR in $\text{D}_2\text{O}$ solution). In the solutions with halide ions the broadening of the signals leads to even fewer N–H stretching modes being resolved in the experimental spectra.

Section B of Table 6.1 (right panel) compares the calculated (OLYP/TZP) data of the $\Lambda^{-}\delta\delta\delta$ molecule with those of the $\Lambda^{-}\delta\delta\delta\cdots{2}\text{Cl}^-$ complex. The angles $\xi$ (between the electric and magnetic dipole transition moments) of the $1E$, $2E$ and $A_2$ modes of the chloride complex are also given in Section B of Table 6.1.

As discussed in reference [84], the $\text{D}_2\text{O}$ solution with acid (DCl) has little hydrogen bonding of the N-H groups to the halide, compared to the DMSO-$d_6$
solution with LiCl, because of strong solvation of the Cl\(^-\) ions in D\(_2\)O, which is absent in DMSO-\(d_6\) which has a much lower dielectric constant and is aprotic. This can be clearly seen when comparing, the experimental IR and VCD intensities measured in DMSO-\(d_6\) solution with excess chloride and those measured in D\(_2\)O solution (see Table 6.1). Thus, in case of the IR intensities a two-fold increase is observed for the \(A_2\) modes, and a significant but not quantifiable increase for the \(E\) modes since those are not observed in the systems without Cl\(^-\) complexation. In the case of VCD, an enhancement of the intensities of 5 up to 133-fold is observed. The intensity enhancements are also accompanied by frequency shifts towards red of about 100-150 cm\(^{-1}\). The same trend is seen also when looking at the calculated data, i.e. upon chloride association an increase in magnitude up to 40-fold is observed for both IR and VCD intensities along with a large redshift of the normal mode frequencies (which are in the range 3260–3320 cm\(^{-1}\) in \(\Lambda-\delta\delta\delta\) and in the range 3015–3148 cm\(^{-1}\) in \(\Lambda-\delta\delta\delta \cdots 2\text{Cl}^-\)).

Figure 6.6 shows a comparison between the experimental VCD spectrum of \(\Lambda-\left[\text{Co(en)}_3\right]^{3+}\) measured in DMSO–\(d_6\) with excess of chloride ions and the
calculated VCD spectra of $\Lambda - \delta \delta \delta - 2\text{Cl}^-$ obtained using OLYP/TZP and B3LYP/LanL2DZ, for the CH/NH stretching region. The B3LYP/LanL2DZ spectrum was taken from reference [55]. As can be seen the experimental and calculated (OLYP and B3LYP) VCD spectra are in very good agreement. Intensity wise, the OLYP/TZP spectrum reproduces the experimental spectrum somewhat better than B3LYP/LanL2DZ spectrum. Frequency wise, the B3LYP functional is somewhat better (the frequencies of the B3LYP and OLYP N$\rightarrow$H$\cdots$Cl stretching modes were scaled by 0.9643 and 1.0766, respectively). We note that a comparison between the experimental IR/VCD spectra measured in D$_2$O and the calculated spectra of the isolated $\Lambda - \delta \delta \delta$ molecule is irrelevant because the experimental spectrum is strongly perturbed as indicated by the low frequency of the N–H stretching modes.

Thus, even though the OLYP functional overestimates both the intensities and the frequency shifts whereas B3LYP underestimates them, we can conclude based on the comparisons done in Table 6.1 and Fig. 6.6, that the DFT calculations give a good description of the phenomena observed experimentally upon chloride association to the $\Lambda - \text{[Co(en)$_3$]}^{3+}$ molecule.

Beside the dramatic effects of chloride complexation on the intensities and frequencies there are two more details that should be pointed out about the data listed in Table 6.1 for the chloride complex. First, although the $A_2$ modes have the largest IR intensities (exp.: 1098 for $A_2$ vs. 792 for $E$; calc.: 1973.8 for $A_2$ vs. 129.4 for $2E$ and 41.1 for $1E$), their absolute VCD intensity is the smallest (exp.: 89 for $A_2$ vs. 200 for $E$; calc.: 67.8 for $A_2$ vs. 296.9 for $2E$ and 244.1 for $1E$). Since $\cos \xi$ is either 1 or $-1$ ($\xi$ is $0^\circ$ or $180^\circ$) and therefore is not influencing the magnitude of the VCD intensities, the very different behavior of the IR and VCD intensities of the $A_2$ mode on the one hand and the $E$ modes on the other hand is rather striking and calls for an explanation. Second, the values of the $\xi$ angles of the three N$\rightarrow$H$\cdots$Cl modes are either $0^\circ$ or $180^\circ$. Thus, these modes are robust modes [78], i.e. the sign of their rotational strengths is accurately predicted by calculations. As seen, the calculated spectra reproduce well the experimental spectrum.

In IR spectroscopy, the enhancement of the intensities is a consequence of the transfer of charge from the associated ions into the N–H bond [79, 80]. As discussed in chapter 4 section 4.4 (Case E) the VCD enhancement has the same origin. However, the different behavior of the $A_2$ intensity with respect to the $E$ intensities in VCD compared to IR already indicates that the explanation in VCD is more complex. We will for the moment take the charge transfer effects in the vibrational motion, i.e. increasing charge transfer from Cl$^-$ into the $\sigma^*(N-H_{axial})$ orbitals during N–H$_{axial}$ stretch, for granted, and we will deal first (in section
6.4. Results and Discussions

6.4.2) with the central topic of this chapter, namely a detailed analysis of how these charge motions affect the electric and magnetic dipole transition moments and therefore the various intensities. Then in the following section (6.4.3) we will turn to a discussion of how exactly the charge density responds to the nuclear motions of the vibrational modes.

6.4.1 Normal mode analysis

The N–H stretching modes of both Λ−δδδ and Λ−δδδ···2Cl− have been analyzed by visualizing their nuclear displacements. In the N–H stretching modes of the bare Λ−δδδ complex both hydrogens attached to a nitrogen atom move (in phase or out of phase) with similar amplitudes. Upon association of the chloride ions the N–H stretching modes of the bare Λ−δδδ system have mixed in such a way that in the resulting modes the equatorial and axial N–H stretches are uncoupled. Thus, in the N−H···Cl modes of the chloride complex we will be investigating only the hydrogen atoms involved in the inter-molecular bond (the axial hydrogens H_{axial} are moving.

Figure 6.7: Schematic representation of the N→H···Cl stretching modes of Λ−δδδ···2Cl−. For the modes 1E and 2E only one of the degenerate mode pair is shown.
Table 6.2: Decomposition of the N↔H···Cl modes 1E, 2E and A₂ of \( \Lambda - \delta \delta \delta \cdots 2\text{Cl}^- \), which are mostly N–H axial stretches, into (axial and equatorial) N–H stretching modes of the \( \Lambda - \delta \delta \delta \) free molecule. The mixing coefficients are inner products between the normalized vector consisting of all \( x, y, z \) nuclear displacements of a mode of the molecular complex (1E, 2E or A₂) with the similar vectors representing the most important modes of the free molecule. The overlaps (inner product squared of a mode of the complex with the linear combination of mode-vectors of the free molecule) are calculated as the sum of the squared mixing coefficients. Only the modes that had a mixing coefficient with absolute value larger than 0.1 are listed.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Mode No.</th>
<th>Coef.</th>
<th>Overlap</th>
</tr>
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<tbody>
<tr>
<td>1E</td>
<td>94</td>
<td>-0.1208</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>-0.1013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>0.6512</td>
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<tr>
<td></td>
<td>97</td>
<td>0.3370</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.2108</td>
<td></td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>0.5140</td>
<td></td>
</tr>
<tr>
<td></td>
<td>103</td>
<td>0.3439</td>
<td></td>
</tr>
<tr>
<td>2E</td>
<td>94</td>
<td>0.4399</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>-0.5688</td>
<td></td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>0.1242</td>
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</tr>
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<td></td>
<td>100</td>
<td>-0.1870</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>101</td>
<td>0.6136</td>
<td></td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>-0.1103</td>
<td></td>
</tr>
<tr>
<td></td>
<td>103</td>
<td>0.1799</td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>98</td>
<td>-0.6970</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>104</td>
<td>0.7118</td>
<td></td>
</tr>
</tbody>
</table>

There are six N↔H···Cl stretching modes, one A₁, one A₂, and two two-fold degenerated modes of \( E \) symmetry (labeled 1E and 2E). Since the complex has \( D_3 \) symmetry, the A₁ mode is IR/VCD inactive and will not be further discussed. A schematic representation of the N↔H···Cl modes 1E, 2E and A₂ is given in Fig. 6.7.

The N–H modes of the free \( \Lambda - \delta \delta \delta \) molecule that mix to form the modes 1E, 2E and A₂ of the complex and their mixing coefficients are given in Table 6.2. As discussed in chapter 5 section 5.3 the mixing coefficients are inner products between the normalized 3\( N \)-dimensional vectors characterizing the modes (which have as components the \( x, y, z \)-displacements of all nuclei) of the complex \( \Lambda - \)
δδδ⋅⋅⋅2Cl\(^-\) of the parent molecule \(\Lambda - \delta\delta\delta\). The modes of \(\Lambda - \delta\delta\delta\cdot\cdot\cdot2\text{Cl}^-\) can almost perfectly be represented as linear combinations of the modes of the free molecule \((\Lambda - \delta\delta\delta)\). This follows from the fact that the inner products between the modes \(1E, 2E\) and \(A_2\) of \(\Lambda - \delta\delta\delta\cdot\cdot\cdot2\text{Cl}^-\) and the corresponding linear combinations of the \(\Lambda - \delta\delta\delta\) modes are practically 1.0 (see Table 6.2).

6.4.2 The enhancement of IR/VCD intensity

**The mechanism of the intensity enhancement**

As shown in chapter 4 section 4.4 (Case E) the mechanism and the magnitude of the enhancement of the IR/VCD intensities can easily be understood by looking at the nuclear and electronic contributions of the total electric and magnetic dipole transition moments.

Table 6.3 gives the nuclear and electronic contributions to the Cartesian components of the dipole transition moments \(\vec{E}_{01}\) and \(\text{Im}[\vec{M}_{01}]\) of the modes \(1E, 2E\) and \(A_2\) of the \(\Lambda - \delta\delta\delta\cdot\cdot\cdot2\text{Cl}^-\) complex, and for comparison, also of the mode 101 of the free \(\Lambda - \delta\delta\delta\), which is an \(E\) mode (that is representative for the modes of the free molecule). As can be seen, the modes of \(E\) symmetry (\(1E, 2E\) and 101) have electric dipole transition moments (EDTM) and magnetic dipole transition moments (MDTM) with non-zero \(x\) and \(y\) Cartesian components and zero \(z\) components, whereas the mode \(A_2\) has non-zero \(z\) components and zero \(x\) and \(y\) components. This can be qualitatively understood by looking at the schematic representation of the nuclear displacement vectors of the modes \(1E, 2E\) and \(A_2\) in Fig. 6.7. In the \(E\) modes a cancelation between the \(z\) components of the displacement vectors of the H atoms occurs at each \(H_{axial}\) triad. This means that no net displacement of charge in the \(z\) direction occurs in the \(E\) modes. In the \(A_2\) modes the cancelation occurs for the \(x\) and \(y\) components of the displacement vectors and as a result no net charge displacement occurs in the \(xy\) plane. This is ultimately a consequence of the \(D_3\) symmetry.

Looking at the non-zero components of the dipole transition moments in Table 6.3, we note a clear difference between the free molecule and the chloride complex. In mode 101 of the free molecule the electronic and nuclear components have different sign and as a result they counteract each other. This holds for both the \(x\) and \(y\) components. We note that since the nuclei and the electrons have opposite electrical charges, this is exactly what one would expect, viz., the displacements of the nuclei induce a displacement of approximately the same amount of negative electronic charge (the nuclei ”drag” the electrons along).

For the chloride complex, the situation is different. Counteraction of electronic
Table 6.3: Cartesian components of the nuclear (nuc.) and electronic (el.) contributions of the electric ($\vec{E}_{01}$) and magnetic (Im[$\vec{M}_{01}$]) transition dipole moments for the modes 1$E$, 2$E$ and $A_2$ of the chloride complex and mode 101 of the free molecule (an $E$ mode). Units: $E_{01}$(10$^{-22}$esu·cm), $M_{01}$(10$^{-24}$esu·cm).

<table>
<thead>
<tr>
<th>Mode</th>
<th>$X$</th>
<th>$Y$</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nuc.</td>
<td>el.</td>
<td>nuc.</td>
</tr>
<tr>
<td>1$E$</td>
<td>$E_{01}$</td>
<td>$-41.37$</td>
<td>$-34.85$</td>
</tr>
<tr>
<td></td>
<td>Im[$\vec{M}_{01}$]</td>
<td>$482.68$</td>
<td>$1780.08$</td>
</tr>
<tr>
<td>2$E$</td>
<td>$E_{01}$</td>
<td>$9.69$</td>
<td>$39.15$</td>
</tr>
<tr>
<td></td>
<td>Im[$\vec{M}_{01}$]</td>
<td>$154.48$</td>
<td>$406.03$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$E_{01}$</td>
<td>$0.00$</td>
<td>$0.00$</td>
</tr>
<tr>
<td></td>
<td>Im[$\vec{M}_{01}$]</td>
<td>$0.00$</td>
<td>$0.00$</td>
</tr>
<tr>
<td>101 of FM ($E$ mode)</td>
<td>$E_{01}$</td>
<td>$-32.93$</td>
<td>$21.46$</td>
</tr>
<tr>
<td></td>
<td>Im[$\vec{M}_{01}$]</td>
<td>$506.96$</td>
<td>$-293.38$</td>
</tr>
</tbody>
</table>

and nuclear contributions is no longer observed. In all cases but one (the $z$ component of Im[$\vec{M}_{01}$] in the $A_2$ mode of the chloride complex) the electronic and nuclear contributions to a Cartesian component have the same sign. Thus, in the chloride complex, the nuclear and electronic components reinforce each other rather than counteracting each other as they do in the free molecule. As a result, the total electric and magnetic dipole transition moments of the complex are much larger than the ones of the free molecule. Since the IR and VCD intensities are determined by the two dipole transition moments, via Eqs. (6.1) and (6.2), respectively, it is clear that both intensities are significantly enhanced upon complexation.

A very simple and intuitive physical explanation can be given for the effects of the complexation described above. When the H atoms move towards the Cl$^-$ ions, the increasing transfer of charge from the chloride ions into the N–H bonds is an opposite movement of negative electronic charge that counteracts the effects of the electrons dragged along by the displaced protons. Thus, depending on the amount of charge that flows into the N–H bonds, the total electronic contributions of the electric dipole transition moments (EDTM) either have much smaller magnitudes and therefore are unable to counteract the nuclear contributions anymore, or change sign and therefore will reinforce the nuclear parts. In both cases the magnitudes of the total EDMI are significantly increased as a consequence of the charge transfer in the chloride complex (due to the suppression of the cancellation of nuclear and electronic parts). Furthermore, since the electric and magnetic phenomena are intimately related, a sign change of the electronic contribution of the EDMI will induce a sign change of the electronic contribution of the (perpendicular) magnetic dipole transition moment (MDTM).
Symmetry constraints on the EDTM and MDTM and the magnitude of IR/VCD intensity

The displacement of the \( H_{axial} \) atoms, as well as the counteracting charge transfer, are in all modes mostly in the positive or negative \( z \) direction. Thus, it is to be expected that the resulting EDTMs will have very large \( z \) components (much larger than the \( x \) and \( y \) components). Furthermore, these large \( z \) components of the EDTMs will induce very large MDTMs in the \( xy \) plane (the plane perpendicular to the \( z \) direction). That is, the \( x \) and \( y \) components of the MDTMs are expected to be much larger than the \( z \) component.

Due to cancelations dictated by symmetry, the close relation between electric and magnetic phenomena cannot be traced per mode in Table 6.3. In the \( E \) modes, since the \( z \) components of the total EDTMs are zero (by symmetry), no net charge displacements along \( z \) that can influence the \( x \) and \( y \) components of the MDTMs are visible. In the \( A_2 \) mode the effects of the \( z \) charge displacements on the \( x \) and \( y \) components of the MDTM are equally invisible, since these components (of the total MDTMs) are also zero by symmetry.

In order to shed additional light on the overall picture deduced from Table 6.3, in the following we will investigate the atomic contributions of the total electric and magnetic dipole transition moments of the modes \( 2E \) and \( A_2 \). The mode \( 1E \) is not considered since it is very similar to the mode \( 2E \). Furthermore, since in the \( N \leftrightarrow H \cdots Cl \) modes the effects of the charge transfer are most notable for the six \( H \) atoms involved in the complex bond to the \( Cl^- \), and since these atoms have the largest displacement vectors, we single out the contributions of these \( H \) atoms for special consideration.

Tables 6.4 and 6.5 show the nuclear and electronic contributions of the atomic EDTMs (upper panels) and MDTMs (lower panels) of these six \( H \) atoms for the normal modes \( 2E \) and \( A_2 \), respectively. The summed contributions of all other atoms as well as the total transition dipole moments are also given.

Considering first the \( A_2 \) mode (Table 6.4), we note that the nuclear \( z \) components of the atomic EDTMs are much larger than the nuclear \( x \) and \( y \) components. This is in keeping with the predominantly \( z \) directed nuclear motions in this mode. The electronic \( z \) components are much reduced due to the counteracting charge transfer motion of the electronic charge, although they still have different sign compared to the nuclear \( z \) components. The sum over all 6 \( H \)'s of \(+47.10\) of the electronic \( z \) components is much smaller than the \(-576.30\) of the nuclear \( z \) components. Combined with the contributions of all the other atoms, which are numerically not negligible, but do have roughly equal nuclear and electronic parts of opposite sign, the nuclear and electronic sum totals are both of the same sign.
Table 6.4: Normal mode $A_2$. The length and the Cartesian components of the nuclear (nuc) and electronic (el) contributions of the atomic EDTMs, $\vec{E}_{01}$ (upper panel), and MDTMs, Im[$\vec{M}_{01}$] (lower panel), of the hydrogen atoms involved in the inter-molecular bond. Contributions of all other atoms as well as the total EDTMs and MDTMs ($\vec{E}_{01}$ and Im[$\vec{M}_{01}$]) are also given. Units: $\vec{E}_{01}$, $\vec{E}_{01}^\lambda$ ($10^{-22}$esu-cm), Im[$\vec{M}_{01}$], Im[$\vec{M}_{01}^\lambda$] ($10^{-24}$esu-cm).

\[
\begin{array}{cccccc}
\text{Atom} & |\vec{E}_{01}| & \text{nuc} & \text{el} & \text{nuc} & \text{el} \\
\hline
\text{H}_26 & 96.02 & -29.84 & 1.86 & -7.71 & -17.91 & -96.05 & 7.85 \\
\text{H}_{30} & 96.02 & 8.24 & -16.44 & 29.70 & 7.34 & -96.05 & 7.85 \\
\text{H}_{34} & 96.02 & 21.60 & 14.58 & -21.99 & 10.56 & -96.05 & 7.85 \\
\text{H}_{28} & 96.02 & -8.24 & 16.44 & 29.70 & 7.34 & -96.05 & 7.85 \\
\text{H}_{32} & 96.02 & 29.84 & -1.86 & -7.71 & -17.91 & -96.05 & 7.85 \\
\text{H}_{36} & 96.02 & -21.60 & -14.58 & -21.99 & 10.56 & -96.05 & 7.85 \\
\hline
\text{other atoms} & 0.00 & 0.00 & 0.00 & 0.00 & -576.30 & 47.10 \\
\text{total $\vec{E}_{01}$} & 556.94 & 0.00 & 0.00 & -556.94 \\
\end{array}
\]

\[
\begin{array}{cccccc}
\text{Atom} & \text{Im}[\vec{M}_{01}] & \text{nuc} & \text{el} & \text{nuc} & \text{el} \\
\hline
\text{H}_26 & 658.08 & 171.36 & 247.74 & -302.64 & -204.71 & -28.94 & 32.96 \\
\text{H}_{30} & 658.06 & -347.77 & -301.15 & 2.92 & -112.18 & -28.94 & 32.96 \\
\text{H}_{34} & 658.06 & 176.41 & 53.41 & 299.72 & 316.90 & -28.95 & 32.96 \\
\text{H}_{28} & 658.06 & 347.77 & 301.15 & 2.92 & -112.18 & -28.94 & 32.96 \\
\text{H}_{32} & 658.06 & -171.36 & -247.74 & -302.64 & -204.71 & -28.94 & 32.96 \\
\text{H}_{36} & 658.06 & -176.41 & -53.41 & 299.72 & 316.90 & -28.95 & 32.96 \\
\hline
\text{6 H's} & 0.00 & 0.00 & 0.00 & 0.00 & -173.64 & 197.76 \\
\text{other atoms} & 0.00 & 0.00 & 0.00 & 0.00 & +120.52 & -49.00 \\
\text{total Im}[\vec{M}_{01}] & 95.64 & 0.00 & 0.00 & 93.64 \\
\end{array}
\]

The $x$ and $y$ components of the atomic EDTMs of the $A_2$ mode are relatively small. The counteracting effect of the charge transfer on the electronic parts is often (though not always) visible for individual atoms, but the $x$ and $y$ EDM components add up to zero by symmetry anyway. The atomic $x$ and $y$ EDM components are too small to induce any changes in the perpendicular ($z$) atomic MDTMs. As a result the atomic $z$ components of the MDTMs are relatively small and have nuclear and electronic parts of different sign and similar magnitude which add up to a small total contribution of the six H atoms (see lower panel of Table 6.4). This makes the contribution from the other atoms to the $z$ component of the MDTM of the $A_2$ mode equally important.

We note that the lack of significant influence of the charge transfer in the complex bond on the MDTM $z$ component of $A_2$ explains the phenomenon ob-
served earlier in Table 6.3. That is, the electronic and nuclear z components of
the MDTM of mode $A_2$ have opposite signs and counteract each other. However,
it should also be noted that the perpendicular $x$ and $y$ atomic MDTMs of the six
H atoms are affected by the large $z$ component of the EDTMs, i.e. the electronic
and nuclear parts have the same sign in almost all cases (the only exception in-
volves a very small nuclear $y$ component of 2.92). These $x$ and $y$ components of
the atomic MDTM are large (compared to the $z$ components), in agreement with
the predominant motion of the charges in the $z$ direction, but since they sum up
to zero, there is no effect on the rotational strength. This explains the magni-
tudes of the IR and VCD intensities of the mode $A_2$. The very large IR intensity
(see Table 6.1) arises from the square of the large $z$ component of $\vec{E}_{01}$. The VCD
intensity on the other hand is determined by the inner product of $(E_{01})_z$ and
$(M_{10})_z$, and although it is enhanced, it is still moderate due the relatively small
$(M_{10})_z$.

For the $2E$ mode the picture is rather similar, only the various Cartesian
components play different roles. In keeping with the predominantly $z$-directed
motion of the atoms in this mode, the $z$ components of the individual atomic
EDTMs are relatively large (compared to the $x$ and $y$ components). Again, as
with the $A_2$ mode, in response to the charge transfer caused by the complexation
of the chloride ions, the electronic parts of the $z$ components have much smaller
magnitudes than their nuclear counterparts, and although the two components
still have opposite signs the electronic contributions are unable to counteract the
nuclear ones. Thus, the magnitudes of the $z$ components of the atomic EDTMs of
the $2E$ mode have increased significantly compared to the free molecule. However,
since in the $2E$ mode the contributions to the $z$ component from the various atoms
cancel, no overall large $z$ component of the total EDTM is obtained, in contrast
to the $A_2$ mode.

Even though the $z$ component of the total EDTM is zero, the charge transfer
effect is still important for the $2E$ mode since the large net $z$ components of the
atomic EDTMs are mirrored in large perpendicular ($x$ and $y$) atomic MDTM
components. The charge transfer effect shows up in that the nuclear and elec-
tronic parts of the atomic MDTMs have mostly the same sign and as a result the
$x$ and $y$ components of the total MDTM are large (see lower panel of Table 6.5).

Turning back to the $x$ and $y$ components of the EDTM, we note that per atom
they are smaller than the $z$ components, but they do not cancel when added over
the atoms. The nuclear and electronic parts have the same sign for most of the
atoms, so they add up. The total $x$ and $y$ EDTM components, although increased,
are much smaller than the $A_2$ $z$ component. Thus, the IR intensity, resulting form
the inner product of $\vec{E}_{01}$ with itself is accordingly considerably lower than the
In this section we investigate the transfer of charge from the associated chloride ions into the N–H bonds induced during the normal mode motion when the H

Table 6.5: Normal mode 2E. The length and the Cartesian components of the nuclear (nuc) and electronic (el) contributions of the atomic EDTMs, $\vec{E}_{01}^A$ (upper panel), and MDTMs, Im[$\vec{M}_{01}^A$] (lower panel), of the hydrogen atoms involved in the inter-molecular bond. Contributions of all other atoms as well as the total EDTMs and MDTMs ($\vec{E}_{01}$ and Im[$\vec{M}_{01}$]) are also given. Units: $\vec{E}_{01}$, $\vec{E}_{01}^A$ (10$^{-22}$ esu·cm), Im[$\vec{M}_{01}$], Im[$\vec{M}_{01}^A$] (10$^{-24}$ esu·cm).

A$_2$ IR intensity (see Table 6.1). The rotational strength, resulting from the inner product of ($E_{01}$) and ($M_{10}$), is however large, on account of the large MDTM $x$ and $y$ components and the not negligible EDM $x$ and $y$ components. We are therefore able to understand both the mechanism of the enhancement of the IR and VCD intensities by the chloride ion complexation, and the relative magnitudes of the IR and VCD intensities of the 2E (and similarly 1E) versus A$_2$ N←H····Cl modes.

6.4.3 The charge transfer

Charge redistribution during vibrational motion

In this section we investigate the transfer of charge from the associated chloride ions into the N–H bonds induced during the normal mode motion when the H
atoms in the intermolecular bond approach the chloride ions.

As an example, the mode $A_2$ will be considered. The six H atoms are displaced by 0.05 Å along their nuclear displacement vectors. Then, a single point calculation is done for this unrelaxed geometry. As can be seen from the schematic representation of the mode $A_2$ in Fig. 6.7, the hydrogens $H_{28}$, $H_{32}$ and $H_{36}$ are displaced towards the $Cl^-_{38}$ ion, whereas the hydrogens $H_{26}$, $H_{30}$ and $H_{34}$ are displaced away from the $Cl^-_{39}$. We note that the displacement considered (0.05 Å) is comparable to the amplitude of the vibrational motion.

An estimation of the amount of charge transferred as a result of the displacement of the protons can be obtained by comparing the Mulliken charges of the two chloride ions in the equilibrium geometry and in the displaced one. In the equilibrium geometry the Mulliken charge of each chloride ion is $-0.5215$ electrons. In the displaced geometry the two chlorides have different Mulliken charges, the charge of the $Cl^-_{38}$ is $-0.4730$ electrons whereas the charge of the $Cl^-_{39}$ is $-0.5640$ electrons. This clearly shows that when the protons approach a $Cl^-$, charge flows from the ion into the N–H bond, whereas when the protons move away from the $Cl^-$ the reverse happens. The resulting effect is charge transfer over effectively a large distance, from $Cl^-_{38}$ towards $Cl^-_{39}$. We have verified that the same conclusions are also obtained when looking at the Hirshfeld charges and/or the Voronoi deformation densities (VDD) charges [105] of the two chloride ions.

The changes in charge transfer during the vibrational motion are largely determined by the N–H$_{axial}$ $\sigma^*$ orbitals. A triad of N–H$_{axial}$ $\sigma^*$ orbitals can form a totally in-phase combination, e.g. $(1/\sqrt{3})(\sigma^*_{28} + \sigma^*_{32} + \sigma^*_{36})$ (see atom numbering in Fig. 6.5), which has $\sigma$ symmetry with respect to the $C_3$ axis and can form a $\sigma$ bond with the $Cl^-_{38} 3p_z$ orbital. The same three local $\sigma^*$ orbitals can also form two combinations which have nodal planes passing through the $z$ axis and which can form donor-acceptor $\pi$ bonds with the $Cl^-_{38} 3p_x$ and $3p_y$ orbitals. Of course the $\sigma^*$s at the triad of axial N–H groups at the negative $z$ axis can form analogous $\sigma$ and $\pi$ combinations, which can interact with the $Cl^-_{39} 3p_z$ and $3p_{x,y}$ orbitals, respectively. In the overall $D_3$ symmetry group these $\sigma$ and $\pi$ orbitals at the upper and lower N-H triads form plus and minus symmetry combinations; the $\sigma$ orbitals for instance form combinations that enter the $A_1$ and $A_2$ irreps and interact with the combinations of the axial $Cl^-$ $3p_z$ donor orbitals of the same irrep symmetry. The $\pi$ orbitals go into the $E$ irrep and interact with $E$ combinations of the $3p_{x,y}$ orbitals at $Cl^-_{38}$ and $Cl^-_{39}$.

An illustration is given for the $\sigma$ case. Figure 6.8 displays in the upper panel the virtual orbitals $14A_1$ and $11A_2$ of $\Lambda-\delta\delta\delta$ at equilibrium geometry, and in the lower panel the corresponding orbitals (66A and 67A) of $\Lambda-\delta\delta\delta$ with displaced hydrogens. These orbitals are clearly formed locally from in phase combinations.
Virtual MOs

Equilibrium Geometry

![Virtual MOs in equilibrium geometry](image1)

Displaced geometry

![Virtual MOs in displaced geometry](image2)

Figure 6.8: The shape of the virtual σ MOs that play an important role in the charge transfer phenomenon.

of the N–H$_{axial}$ σ* orbitals at an H$_{axial}$ triad, so that lobes with large amplitude towards the Cl$^-$ ions are created.

Upon displacement of the six H atoms, a localization of the orbitals occurs. The (localized) virtual orbitals 66A and 67A of Λ − δδδ with displaced hydrogens are in phase and out of phase, respectively, combinations of the virtual orbitals 14A$_1$ and 11A$_2$. The 14A$_1$ and 11A$_2$ orbitals are close in energy and can easily be mixed by perturbations such as the H displacements. As can be seen in Fig. 6.8, orbital 66A (the out of phase combination) is localized on the upper three N–H
bonds that have been stretched, and it will overlap with chloride ion Cl\(^{-}\)\(_{38}\), whereas orbital 67\(A\) (the in phase combination) is localized mostly on the downside H’s of the three N–H bonds that have been shortened, and will overlap with chloride ion Cl\(^{-}\)\(_{39}\). The stretching of the upper N–H bonds will cause a lower energy of orbital 66\(A\), and better overlap with Cl\(^{-}\)\(_{38}\) since its amplitude towards the Cl\(^{-}\)\(_{38}\) is somewhat extended, while the shortening of the lower N–H bonds will raise the energy of 67\(A\) and its slight shrinking will lower the overlap with Cl\(^{-}\)\(_{39}\). This means that more charge will be donated by the chloride Cl\(^{-}\)\(_{38}\) into the virtual orbital 66\(A\), whereas less charge will be donated by the chloride Cl\(^{-}\)\(_{39}\) into 67\(A\). Precisely the same effects operate in the \(\pi\) symmetry. This explains the effects on the Cl\(^{-}\) charges of the H displacements in the vibrational motion that we noted above.

**Contributions from the occupied MOs to the AATs and APTs**

In order to further substantiate that the observed large effect of complexation on the intensities of the N-H\(_{axial}\) modes originates from charge transfer, we will show in this section that the observed effects on the electronic contributions to the EDTMs and MDTMs can be traced back to the role of the Cl\(^{-}\) 3p donor orbitals. The electronic contributions of both atomic tensors (APT and AAT) can be decomposed into contributions from the occupied molecular orbitals, see Eqs. (3.10) and (3.13). We have monitored how the electronic contributions of the atomic tensors (APT and AAT) of the H atoms in the intermolecular bond and their MO contributions change when going from the free molecule to the chloride complex. We have found that in most of the cases when a tensor component has significantly different values in the free molecule and in the complex, the contributions from the 8 occupied Cl\(^{-}\) valence orbitals of the complex (3s and 3p orbitals) have relatively large magnitudes. To substantiate this remark, in the following we will discuss the case of two tensor components (\(xz\) and \(zx\)) of the AAT of the hydrogen H\(_{28}\) in Fig. 6.5 (the tensor is not symmetrical). In the \(zx\) tensor component the contributions from the 8 Cl\(^{-}\) based occupied MOs have large magnitudes, whereas for the \(xz\) tensor component they are almost zero. We note that we have analyzed the MO contributions of all the tensor components of both APTs and AATs, however, for brevity and due to the qualitative nature of the analysis we shall discuss here only two representative examples.

Figures 6.9 show the contributions from all occupied MOs to the tensor components \(I_{xz}^{28}\) and \(I_{zx}^{28}\), respectively. The vertical axis indicates the magnitude of the MO contributions, \(I_{\alpha\beta}^{28}(J_{\text{occ}})\), while the horizontal axis indicates the occupied MOs (\(J_{\text{occ}}\)). The (mainly) Cl\(^{-}\) orbitals, which have no counterparts in the free
molecule, have been assembled to the right (orbitals 64-81). The orbitals 64-73 are core orbitals of Cl\(^-\), whereas the orbitals 74-81 are the 3s, 3p orbitals of Cl\(^-\). The rest of the occupied orbitals (1-63) are orbitals of the bare \(\Lambda\).

The tensor component \(I_{xz}^{28}\) has similar values in the complex (−0.559 a.u.) and in the free molecule (−0.629 a.u.), and as can be seen in Fig. 6.9 (left panel) the contributions of the last 8 occupied MOs are almost zero (note the different vertical scale of the left and right panels of Fig. 6.9). The tensor component \(I_{zx}^{28}\), on the other hand, has very different values in the complex (−0.789 a.u.) and in the free molecule (+0.7097 a.u.), and as can be seen in Fig. 6.9 (right panel) the contributions due to the last 8 occupied MOs have significant magnitudes and mainly determine this difference. Since this correlation with significant Cl\(^-\) orbital contributions can be made for almost all tensor components that show substantial changes, we conclude that the occupied Cl\(^-\) valence orbitals i.e. MOs 74-81, play a key role in the changes observed in the \(H_{axial}\) atomic tensors, hence in the total electric and magnetic transition dipoles and therefore in the enhancement mechanism. This is in complete accord with the role of charge transfer out of these Cl\(^-\) orbitals we have inferred earlier. Thus, we conclude that the analysis of the MO contributions to the atomic tensors presented in this section quantifies the charge transfer effects and demonstrates explicitly the direct involvement of the chloride occupied valence orbitals in the enhancement of the IR and VCD
6.5 Summary and Conclusions

In this chapter we have investigated the enhancement of the IR and VCD intensities of the N–H stretching modes of [Co(en)$_3$]$^{3+}$ induced by the association of the chloride ions. We have shown that due to the charge transfer from the chloride ions into the N–H bond, the electronic parts of both the electric and magnetic dipole vibrational transition moments often change sign. As a result the nuclear and electronic parts reinforce each other (normally they counteract each other) which results in enhancement of the intensities.

We note that since the charge transfer affects both the electric and magnetic dipole transition moments (EDTM and MDTM), the mechanisms responsible for the enhancement of the IR and VCD intensities are related. However, as the discussion of the $A_2$ and $2E$ N$\rightarrow$H$\cdots$Cl modes showed, the effects may show up in different Cartesian components of the EDTM and the MDTM. Large $z$ directed charge flow affects the $z$ component of the EDTM, and if that is not zero by symmetry, there is a large effect on the IR intensity, as in the $A_2$ mode. But since this charge flow does not increase the $z$ component of the MDTM, the inner product of EDTM and MDTM (consisting only of the product of the $z$ components) shows a moderate effect, hence moderate enhancement of the VCD intensity. The perpendicular ($x$ and $y$) MDTM components are related to $z$ charge flow, and in the $E$ modes in which these $x$ and $y$ components are nonzero, the large $x$ and $y$ MDTM components cause a relatively large VCD intensity.

Our analysis has provided a simple and intuitive overall physical picture of the mechanism responsible for the enhancement of both IR and VCD intensities, clearly explaining the origin of very large enhancements (up to 3 orders of magnitude [79, 80]), which have been known for a long time in the case of IR intensities.

We have also shown the N–H stretching modes (N$\rightarrow$H$\cdots$Cl) are robust modes (as defined in the chapters 4 and 5) [78], with values of the angle $\xi$ (made by their electric and magnetic dipole transition moments) that differ far from 90°, being either 0° or 180°. This is a consequence of the $D_3$ symmetry. As a result their signs are accurately predicted by calculations, and therefore good agreement is expected between calculations and experiments. The comparisons between the calculated (OLYP/TZP and B3LYP/LanL2DZ) VCD spectrum of the [Co(en)$_3$]$^{3+}$ $\cdots$2Cl$^-$ in the $\Lambda - \delta\delta\delta$ conformation and the experimental spectrum of [Co(en)$_3$]$^{3+}$ measured in excess of chloride ions (taken from reference [55])

intensities via an electronic mechanism.
showed that this is indeed the case.

We have applied the analysis of the APTs and AATs in terms of contributions from the occupied molecular orbitals we have introduced in chapter 4 [78]. This has helped to identify the charge transfer from the Cl\(^{-}\) orbitals as the cause of the intensity enhancements we have considered in this paper. Such an analysis should be more widely applicable, and for instance also provide insight into other electronic effects that affect the VCD spectra, such as the effects induced by d-electron configuration of a central metal ion [84, 106, 107].