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Raman optical activity spectra of chiral transition metal complexes

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Dedicated to Professor P. Botschwina on the occasion of his 60th birthday.

Abstract

We present calculated vibrational Raman optical activity (ROA) spectra for the transition metal complexes *A*-tris(acetylacetonato)-cobalt(III), *A*-tris(acetylacetonato)rhodium(III), dichloro-(6*R*,7*S*,9*S*,11*S*-(–)-sparteine)zinc(II) and $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)-cobalt(III). For this study, it was necessary to benefit from density-fitting techniques to a large extent. Necessary implementations are described and the gauge origin problem is addressed. The importance of the electric-dipole–electric-quadrupole polarizability tensor for ROA intensity differences is investigated and found to be small, especially at lower wavenumbers where no C–H stretching vibrations occur. Furthermore, the basis set and density functional dependence is examined.

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Keywords: Optical activity; Raman spectroscopy; Density functional calculations; Vibrational spectroscopy

1. Introduction

Stereochemistry is an important aspect in chemistry, influencing strongly certain properties of molecules. There are several techniques in order to gain information about the chirality of systems, among them being the promising, quite young technique of vibrational Raman optical activity (ROA) spectroscopy [1–4]. Usually, the intensity differences of the Raman intensities scattered by the molecules in incident right- and left-circularly polarized light are measured [5]. For the assignment of ROA spectra [6,7], quantum chemical calculations are required (see Ref. [8] for a recent review on the *first-principles* calculation of vibrational spectra), because no universal relationship between molecular structure and intensity differences is known yet [9–12].

ROA experiments have been performed for polymers, peptides, and even for large systems like proteins and viruses (see, e.g. Refs. [13–21]), which can be studied in their natural environment. ROA calculations, however, are very

time-consuming and therefore full ROA spectra have only been evaluated for quite small organic molecules (compare, for example, Refs. [22–30]). The largest molecule investigated so far with density functional theory (DFT) is decalalanine [29]. ROA spectra of chiral metal complexes have not been reported at all, in contrast to vibrational circular dichroism (VCD) spectra [31–33]. Motivated by these VCD measurements and the expectation that ROA measurements will follow, we present the first ROA calculations of metal complexes. Our goal is to assess the feasibility of such calculations and to uncover possible pitfalls. We have chosen several closed-shell complexes with different ligands and metal atoms (see Fig. 1): first, *A*-tris(acetylacetonato)cobalt(III) and *A*-tris(acetylacetonato)rhodium(III), for which recently VCD measurements have been reported [31], furthermore dichlorosparteinezinc(II) (sparteine is an abbreviation for 6*R*,7*S*,9*S*,11*S*-(–)-sparteine (compare Ref. [32]) and $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III) (for an explanation of the nomenclature and for references to VCD measurements and calculations, see Ref. [34]).

In order to reduce the computational effort, we will rely on density-fitting techniques [35] for the calculation of the

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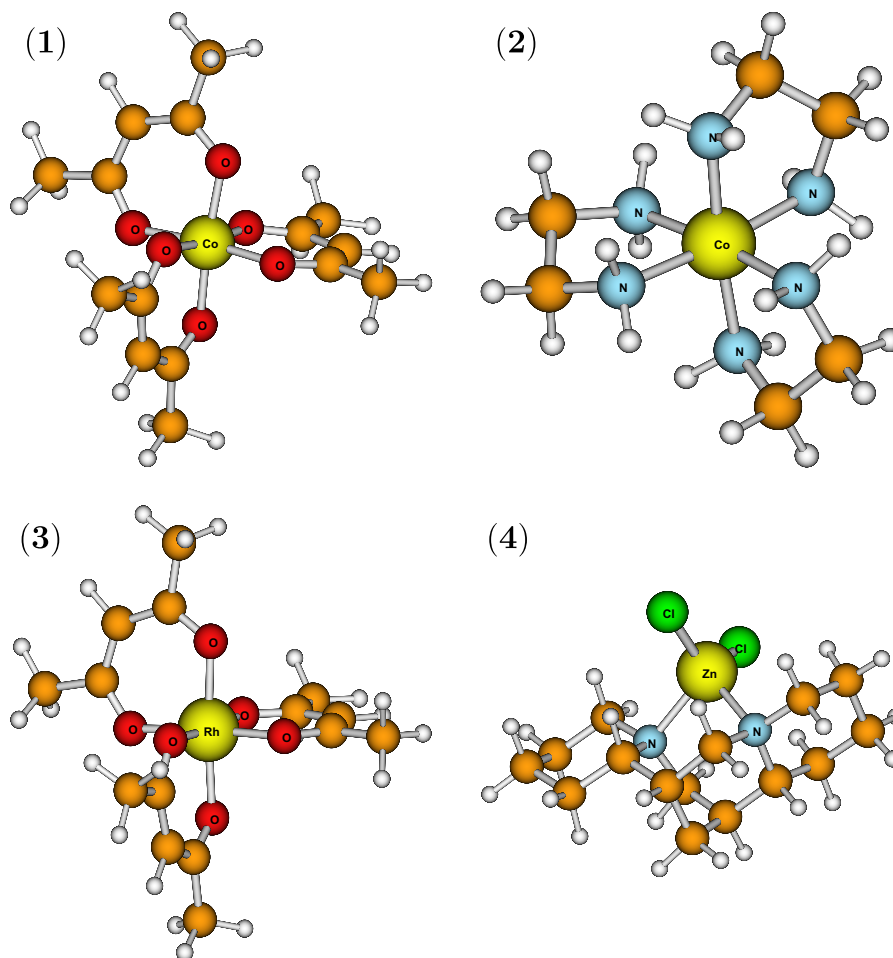


Fig. 1. Optimized structures (DFT(BP86/RI)/TZVP) of *A*-tris(acetylacetonato)cobalt(III) (1) (top, left-hand side), *A*($\delta\delta\delta$)-tris(ethylenediamine)cobalt(III) (2) (top, right-hand side), *A*-tris(acetylacetonato)rhodium(III) (3) (bottom, left-hand side) and dichloro(sparteine)zinc(II) (4) (bottom, right-hand side).

property tensors and the vibrational frequencies. For the latter, the harmonic approximation has been employed since evaluation of anharmonic contributions is computationally expensive and feasible only for small systems (for illustrative examples, we may refer the reader to Refs. [36–38] of the work of Botschwina).

This work is organized as follows: After a brief introduction to the theory of ROA spectroscopy with a focus on the origin dependence of ROA invariants in Section 2, the presentation of the computational methodology follows in Section 3. The basis set and density functional dependence is analyzed in Section 4. Afterwards, calculated spectra are discussed in Section 5. Finally, the results are summarized and an outlook is given in Section 6.

2. Theory of ROA spectroscopy

In order to provide the notation required for this work, a brief introduction into the theory of ROA is given. The ROA intensity differences can be measured in distinct experimental set-ups. Due to the good signal-to-noise ratio [4], a scattering angle of 180° (so-called backscattering) is mostly employed. In the case of ROA spectroscopy

employing incident circularly polarized light, the intensity difference is given as [39,40]

$$(I^R - I^L)(180^\circ) \propto 96 \left[\beta(\mathbf{G}')^2 + \frac{1}{3} \beta(\mathbf{A})^2 \right], \quad (1)$$

where the anisotropic invariants $\beta(\mathbf{G}')^2 = \frac{1}{2}(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta})$ and $\beta(\mathbf{A})^2 = \frac{1}{2}\omega_L\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma,\delta\beta}$ are needed. Hartree atomic units are used throughout this work and summation over repeated Greek indices is implied, whereby Greek subscripts refer to the x , y and z components. $\epsilon_{\alpha\beta\gamma}$ is the $\alpha\beta\gamma$ component of the third-rank antisymmetric (Levi-Civita) unit tensor and ω_L is the wavelength of the incident light. For other scattering angles like 0° , also the isotropic invariant $\alpha G' = \frac{1}{9}\alpha_{\alpha\alpha}G'_{\alpha\alpha}$ is required. The tensor components $\alpha_{\alpha\beta}$, $G'_{\alpha\beta}$ and $A_{\alpha,\beta\gamma}$ can be written as [3]

$$\alpha_{\alpha\beta} = 2 \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \hat{\mu}_\alpha | j \rangle \langle j | \hat{\mu}_\beta | n \rangle), \quad (2)$$

$$G'_{\alpha\beta} = -2 \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}^2 - \omega_L^2} \text{Im}(\langle n | \hat{\mu}_\alpha | j \rangle \langle j | \hat{m}_\beta | n \rangle), \quad (3)$$

$$A_{\alpha,\beta\gamma} = 2 \sum_{j \neq n} \frac{\omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \hat{\mu}_\alpha | j \rangle \langle j | \hat{\theta}_{\beta\gamma} | n \rangle). \quad (4)$$

α is the electric-dipole–electric-dipole polarizability, \mathbf{G}' the electric-dipole–magnetic-dipole polarizability, known as “ \mathbf{G}' tensor”, and \mathbf{A} the electric-dipole–electric-quadrupole polarizability, the so-called “ \mathbf{A} tensor”. $|n\rangle$ and $|j\rangle$ denote the initial and excited state (total) wave functions and $\omega_{jn} = \omega_j - \omega_n = E_j - E_n$ is their energy separation.

The electric-dipole, magnetic-dipole and electric-quadrupole operators needed in Eqs. (2)–(4) are usually defined as [39]

$$\hat{\mu}_\alpha = - \sum_i r_{i\alpha}, \quad (5)$$

$$\hat{m}_\alpha = - \sum_i \frac{1}{2} \epsilon_{\alpha\beta\gamma} r_{i\beta} p_{i\gamma}, \quad (6)$$

$$\hat{\theta}_{\alpha\beta} = - \frac{1}{2} \sum_i (3r_{i\alpha} r_{i\beta} - r_i^2 \delta_{\alpha\beta}), \quad (7)$$

where the so-called *length representation* of the electric-dipole operator has been chosen and the sum runs over the number of electrons. \mathbf{r}_i (with components $r_{i\alpha}, r_{i\beta}, r_{i\gamma}$) is the position operator, \mathbf{p}_i (with components $p_{i\alpha}, p_{i\beta}, p_{i\gamma}$) the momentum operator of electron i and $\delta_{\alpha\beta}$ is the $\alpha\beta$ component of the second-rank symmetric unit tensor (Kronecker delta).

It should be noted that the theory given here is a consequence of several approximations like the assumption of real wave functions, the neglect of antisymmetric tensor parts and the application of Placzek’s polarizability theory [41]. Furthermore, it is assumed that the molecules are in nondegenerate ground states and that the frequency of the exciting radiation is far away from any absorption frequency of the scattering system. The case of (near) resonance has been investigated by Nafie [42,43] and by Jensen et al. [44]. They found in the limit of the resonance with a single excited state that the intensity differences are monosignate, with the same sign as the corresponding electronic circular dichroism band at the employed wavelength.

2.1. Origin dependence

For the implementational part of this work it is necessary to reconsider the gauge origin dependence of the \mathbf{G}' and \mathbf{A} tensors. As is evident from Eq. (1), the ROA intensity differences are proportional to $b_1 \alpha \mathbf{G}' + b_2 \beta (\mathbf{G}')^2 + b_3 \beta (\mathbf{A})^2$, where the coefficients b_1 , b_2 and b_3 are unrelated to each other. These coefficients adopt different values depending on the experimental conditions. As a consequence, each invariant must be gauge independent individually.

Shifting the coordinate origin from \mathbf{O} to $\mathbf{O} + \mathbf{a}$ (or equivalently, the electron coordinates from \mathbf{r} to $(\mathbf{r} - \mathbf{a})$ with \mathbf{a} having components $a_{i\alpha}$, $a_{i\beta}$ and $a_{i\gamma}$ in the case of electron i , whereby the α , β and γ components have the same value for each electron, the electric-dipole and the magnetic-dipole transition moments transform in the length representation like [3,45]

$$\begin{aligned} \langle n | \hat{\mu}_\alpha(\mathbf{O} + \mathbf{a}) | j \rangle &= - \left\langle n \left| \sum_i [r_{i\alpha} - a_{i\alpha}] \right| j \right\rangle \\ &= - \left\langle n \left| \sum_i r_{i\alpha} \right| j \right\rangle + \sum_i a_{i\alpha} \langle n | j \rangle \\ &= \langle n | \hat{\mu}_\alpha(\mathbf{O}) | j \rangle \quad \forall n \neq j, \end{aligned} \quad (8)$$

$$\begin{aligned} \langle n | \hat{m}_\alpha(\mathbf{O} + \mathbf{a}) | j \rangle &= - \left\langle n \left| \sum_i \frac{1}{2} \epsilon_{\alpha\beta\gamma} (r_{i\beta} - a_{i\beta}) p_{i\gamma} \right| j \right\rangle \\ &= - \left\langle n \left| \sum_i \frac{1}{2} (\mathbf{r}_i \times \mathbf{p}_i)_\alpha \right| j \right\rangle \\ &\quad + \left\langle n \left| \sum_i \frac{1}{2} (\mathbf{a}_i \times \mathbf{p}_i)_\alpha \right| j \right\rangle \\ &= \langle n | \hat{m}_\alpha(\mathbf{O}) | j \rangle + \left\langle n \left| \sum_i \frac{1}{2} (\mathbf{a}_i \times \mathbf{p}_i)_\alpha \right| j \right\rangle \\ &\quad \forall n \neq j. \end{aligned} \quad (9)$$

Analogously, it can be shown that the transition moment containing the electric-quadrupole operator as defined in Eq. (7) changes according to [3,46]

$$\begin{aligned} \langle n | \hat{\theta}_{\alpha\beta}(\mathbf{O} + \mathbf{a}) | j \rangle &= - \left\langle n \left| \frac{1}{2} \sum_i (3(r_{i\alpha} - a_{i\alpha})(r_{i\beta} - a_{i\beta}) \right. \right. \\ &\quad \left. \left. - (\mathbf{r}_i - \mathbf{a}_i)^2 \delta_{\alpha\beta}) \right| j \right\rangle \\ &= \langle n | \hat{\theta}_{\alpha\beta}(\mathbf{O}) | j \rangle - \frac{3}{2} a_\alpha \langle n | \hat{\mu}_\beta(\mathbf{O}) | j \rangle \\ &\quad - \frac{3}{2} a_\beta \langle n | \hat{\mu}_\alpha(\mathbf{O}) | j \rangle + a_\gamma \langle n | \hat{\mu}_\gamma(\mathbf{O}) | j \rangle \delta_{\alpha\beta} \\ &\quad \forall n \neq j. \end{aligned} \quad (10)$$

The property tensors with the shifted origin $\mathbf{O} + \mathbf{a}$ then result as [3]

$$\alpha_{\alpha\beta}(\mathbf{O} + \mathbf{a}) = \alpha_{\alpha\beta}(\mathbf{O}) \quad (11)$$

and

$$\begin{aligned} G'_{\alpha\beta}(\mathbf{O} + \mathbf{a}) &= G'_{\alpha\beta}(\mathbf{O}) - \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}^2 - \omega_L^2} \text{Im} \\ &\quad \times \left(\langle n | \hat{\mu}_\alpha(\mathbf{O}) | j \rangle \left\langle j \left| \sum_i (\mathbf{a}_i \times \mathbf{p}_i)_\beta \right| n \right\rangle \right). \end{aligned} \quad (12)$$

Employing the many-electron Hamiltonian $\hat{H}(\{\mathbf{r}_k\})$ in relation

$$\langle j | [\mathbf{r}_i, \hat{H}(\{\mathbf{r}_k\})] | n \rangle = \omega_{nj} \langle j | \mathbf{r}_i | n \rangle, \quad (13)$$

which holds for eigenstates (see also Refs. [47–49]), and the operator identity [48–50]

$$[\mathbf{r}_i, \hat{H}(\{\mathbf{r}_k\})] = [\mathbf{r}_i, p_i^2/2] = [\mathbf{r}_i, \mathbf{p}_i] \mathbf{p}_i = i \mathbf{p}_i, \quad (14)$$

we obtain

$$\begin{aligned} \langle j | \mathbf{p}_i | n \rangle &= i^{-1} \langle j | [\mathbf{r}_i, \mathbf{p}_i] \mathbf{p}_i | n \rangle = i^{-1} \langle j | [\mathbf{r}_i, \hat{H}(\{\mathbf{r}_k\})] | n \rangle \\ &= i^{-1} \omega_{nj} \langle j | \mathbf{r}_i | n \rangle = i \omega_{jn} \langle j | \mathbf{r}_i | n \rangle. \end{aligned} \quad (15)$$

Then, the origin dependence of $G'_{\alpha\beta}$ can be re-written as

$$\begin{aligned} G'_{\alpha\beta}(\mathbf{O} + \mathbf{a}) &= G'_{\alpha\beta}(\mathbf{O}) + \sum_{j \neq n} \frac{\omega_L \omega_{jn}}{\omega_{jn}^2 - \omega_L^2} \text{Re}(\langle n | \hat{\mu}_\alpha(\mathbf{O}) | j \rangle \\ &\quad \times \langle j | (\mathbf{a} \times \hat{\mu})_\beta | n \rangle) \\ &= G'_{\alpha\beta}(\mathbf{O}) + \frac{1}{2} \omega_L \epsilon_{\beta\gamma\delta} a_\gamma \alpha_{\alpha\delta}(\mathbf{O}). \end{aligned} \quad (16)$$

The \mathbf{A} tensor is also origin dependent,

$$\begin{aligned} A_{\alpha,\beta\gamma}(\mathbf{O} + \mathbf{a}) &= A_{\alpha,\beta\gamma}(\mathbf{O}) - \frac{3}{2} a_\beta \alpha_{\alpha\gamma}(\mathbf{O}) - \frac{3}{2} a_\gamma \alpha_{\alpha\beta}(\mathbf{O}) \\ &\quad + a_\delta \alpha_{\alpha\delta}(\mathbf{O}) \delta_{\beta\gamma}. \end{aligned} \quad (17)$$

If the invariants $\beta(\mathbf{A})^2$, $\beta(\mathbf{G}')^2$ and $\alpha G'$ are calculated, the origin dependence cancels provided that the tensors α , \mathbf{G}' and \mathbf{A} transform as in Eqs. (11), (16) and (17), respectively. The tensors α and \mathbf{A} transform according to Eqs. (11) and (17) also in the case of a finite basis set, which leads to a gauge origin independent $\beta(\mathbf{A})^2$ invariant [48] whether or not the basis set limit is achieved. However, Eq. (16) written for many-electron eigenstates becomes invalid for trial wave functions (like Slater determinants) since Eq. (15) does not hold exactly because Eq. (13) is no longer fulfilled. This translates into the issue of incomplete one-electron basis sets [49, p. 87] in time-dependent DFT (TD-DFT) [51], which in turn leads to gauge origin dependent $\alpha G'$ and $\beta(\mathbf{G}')^2$ invariants.

The gauge error is a function of the distance between gauge and wave function origin [52]. Nowadays, mostly London atomic orbitals [53] are employed for variational wave functions which give gauge origin independent ROA intensity differences.

Another option for obtaining gauge origin independent results is the utilization of the electric-dipole operator in the *velocity representation* $\hat{\mu}^p$ instead of the length representation $\hat{\mu}$, in analogy to Eq. (15),

$$\langle n | \hat{\mu}_\alpha | j \rangle = i\omega_{jn}^{-1} \left\langle n \left| \sum_i p_{ix} \right| j \right\rangle = i\omega_{jn}^{-1} \langle n | \hat{\mu}_\alpha^p | j \rangle. \quad (18)$$

The velocity representation of the electric-quadrupole operator $\hat{\theta}^p$ is calculated via $\omega_{nj} \langle j | \mathbf{r}_i \mathbf{r}_i | n \rangle = \langle j | [\mathbf{r}_i \mathbf{r}_i, \hat{H}(\{\mathbf{r}_k\})] | n \rangle = i \langle j | \mathbf{p}_i \mathbf{r}_i + \mathbf{r}_i \mathbf{p}_i | n \rangle$ [54–57] as

$$\begin{aligned} \langle j | \hat{\theta}_{\alpha\beta}^p | n \rangle &= -(i\omega_{jn})^{-1} \left\langle j \left| \sum_i [p_{ix} r_{i\beta} + r_{i\beta} p_{ix}] \right| n \right\rangle \\ &= (i\omega_{jn})^{-1} \langle j | \hat{\theta}_{\alpha\beta}^p | n \rangle. \end{aligned} \quad (19)$$

If the coordinate origin is altered from \mathbf{O} to $\mathbf{O} + \mathbf{a}$, the electric-quadrupole operator in the velocity representation transforms like

$$\begin{aligned} \langle n | \hat{\theta}_{\alpha\beta}^p(\mathbf{O} + \mathbf{a}) | j \rangle &= \langle n | \hat{\theta}_{\alpha\beta}^p(\mathbf{O}) | j \rangle - a_\alpha \langle n | \hat{\mu}_\beta^p(\mathbf{O}) | j \rangle \\ &\quad - a_\beta \langle n | \hat{\mu}_\alpha^p(\mathbf{O}) | j \rangle \quad \forall n \neq j. \end{aligned} \quad (20)$$

The property tensors in the velocity representation are then obtained as

$$\alpha_{\alpha\beta}^p = 2 \sum_{j \neq n} \frac{1}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \text{Re}(\langle n | \hat{\mu}_\alpha^p | j \rangle \langle j | \hat{\mu}_\beta^p | n \rangle), \quad (21)$$

$$G'_{\alpha\beta}^p = -2 \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \text{Re}(\langle n | \hat{\mu}_\alpha^p | j \rangle \langle j | \hat{m}_\beta | n \rangle), \quad (22)$$

$$A_{\alpha,\beta\gamma}^p = 2 \sum_{j \neq n} \frac{1}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \text{Re}(\langle n | \hat{\mu}_\alpha^p | j \rangle \langle j | \hat{\theta}_{\beta\gamma}^p | n \rangle). \quad (23)$$

The electric-dipole–electric-dipole tensor α^p is obviously gauge origin independent if the coordinate origin is moved from \mathbf{O} to $\mathbf{O} + \mathbf{a}$ because the momenta \mathbf{p}_i do not change:

$$\alpha_{\alpha\beta}^p(\mathbf{O} + \mathbf{a}) = \alpha_{\alpha\beta}^p(\mathbf{O}). \quad (24)$$

The \mathbf{G}'^p and \mathbf{A}^p tensors are origin dependent:

$$\begin{aligned} G'_{\alpha\beta}^p(\mathbf{O} + \mathbf{a}) &= G'_{\alpha\beta}^p(\mathbf{O}) + \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \\ &\quad \times \text{Re} \left(\left\langle n \left| \sum_i p_{ix} \right| j \right\rangle \left\langle j \left| \sum_i (\mathbf{a}_i \times \mathbf{p}_i)_\beta \right| n \right\rangle \right) \\ &= G'_{\alpha\beta}^p(\mathbf{O}) + \frac{1}{2} \omega_L \epsilon_{\beta\gamma\delta} a_\gamma \alpha_{\alpha\delta}^p(\mathbf{O}), \end{aligned} \quad (25)$$

$$A_{\alpha,\beta\gamma}^p(\mathbf{O} + \mathbf{a}) = A_{\alpha,\beta\gamma}^p(\mathbf{O}) - a_\beta \alpha_{\alpha\gamma}^p(\mathbf{O}) - a_\gamma \alpha_{\alpha\beta}^p(\mathbf{O}). \quad (26)$$

However, the gauge origin dependence of the invariants $\alpha G'$, $\beta(\mathbf{G}')^2$ and $\beta(\mathbf{A})^2$ turns out to vanish if the tensors α , \mathbf{G}' and \mathbf{A} are given in the velocity representation and thus transform according to Eqs. (24)–(26) (see Appendix for an explicit demonstration of the gauge origin independence of $\beta(\mathbf{G}')^2$). This is even true in the case of *finite* basis sets.

It should be mentioned that the $\alpha G'$ invariant is also origin independent if it is obtained by the electric-dipole–electric-dipole tensor in the length representation, α , and the electric-dipole–magnetic-dipole tensor in the velocity form, \mathbf{G}'^p . For the calculation of $\alpha G'$, only the trace of \mathbf{G}'^p is needed which is always origin independent because the term which arises due to the origin shift is zero [11,58]:

$$\begin{aligned} G'_{\alpha\alpha}^p(\mathbf{O} + \mathbf{a}) &= G'_{\alpha\alpha}^p(\mathbf{O}) + \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \\ &\quad \times \text{Re} \left(\left\langle n \left| \sum_i p_{ix} \right| j \right\rangle \left\langle j \left| \sum_i (\mathbf{a}_i \times \mathbf{p}_i)_\alpha \right| n \right\rangle \right) \\ &= G'_{\alpha\alpha}^p(\mathbf{O}) + \sum_{j \neq n} \frac{\omega_L}{\omega_{jn}(\omega_{jn}^2 - \omega_L^2)} \\ &\quad \times \text{Re} \left[a_{ix} \left(\left\langle n \left| \sum_i p_{ix} \right| j \right\rangle \left\langle j \left| \sum_i p_{iy} \right| n \right\rangle \right. \right. \\ &\quad \left. \left. - \left\langle n \left| \sum_i p_{iy} \right| j \right\rangle \left\langle j \left| \sum_i p_{ix} \right| n \right\rangle \right) \right. \\ &\quad \left. + a_{iy} \left(\left\langle n \left| \sum_i p_{ix} \right| j \right\rangle \left\langle j \left| \sum_i p_{iz} \right| n \right\rangle \right. \right. \\ &\quad \left. \left. - \left\langle n \left| \sum_i p_{iz} \right| j \right\rangle \left\langle j \left| \sum_i p_{ix} \right| n \right\rangle \right) \right] \end{aligned}$$

$$+a_{iz} \left(\left\langle n \left| \sum_i p_{iy} \right| j \right\rangle \left\langle j \left| \sum_i p_{ix} \right| n \right\rangle - \left\langle n \left| \sum_i p_{ix} \right| j \right\rangle \left\langle j \left| \sum_i p_{iy} \right| n \right\rangle \right) = G'_{xx}(\mathbf{O}). \quad (27)$$

In summary, all ROA invariants are gauge origin independent if the corresponding property tensors are calculated in the velocity representation [44]. Alternatively, α^p and \mathbf{G}^p may be used to calculate $\beta(\mathbf{G}')^2$ whereas $\beta(\mathbf{A})^2$ can also be obtained in the origin-invariant length representation. $\alpha\mathbf{G}'$ is origin independent if \mathbf{G}^p is employed both in combination with α and α^p .

3. Computational methodology and implementations

The molecular structures of all complexes under consideration have been optimized with the quantum chemical program package TURBOMOLE [59] employing the BP86 density functional [60,61] and Ahlrichs' TZVP basis set [62]. For the calculation of the ROA spectra, we used the vibrational spectroscopy package SNF [63,64] in combination with a local version of TURBOMOLE 5.7.1.

The output files of TURBOMOLE do not directly provide values for the \mathbf{G}' tensor. However, TURBOMOLE's module ESCF calculates frequency-dependent polarizabilities and rotatory dispersions. The term rotatory dispersion refers to the measurement of rotation of the polarization plane as a function of the wavelength of the incident light [65]. The trace of the \mathbf{G}' tensor is related to the optical rotation parameter $\beta(\omega_L)$ [66],

$$\beta(\omega_L) = -\frac{1}{3\omega_L} (G'_{xx} + G'_{yy} + G'_{zz}). \quad (28)$$

The off-diagonal values of the rotatory dispersion are also provided by the output file of the ESCF module. Thus, it is easy to calculate the \mathbf{G}' tensor values by multiplication of the optical rotation dispersion values with the laser wavelength. But, the \mathbf{A} tensor is not provided by the ESCF module at all and was therefore implemented into our local version of the ESCF module. In the density matrix formulation of TD-DFT, $\alpha_{\alpha\beta}$ is given as (compare Ref. [67])

$$\alpha_{\alpha\beta} = \langle \mu_\alpha | (\mathbf{A} - \omega_L \mathbf{A})^{-1} | \mu_\beta \rangle, \quad (29)$$

where $\langle \mu_\alpha |$ and $| \mu_\beta \rangle$ are the α and β components of the electric-dipole moment operator in the basis of unperturbed molecular Kohn–Sham orbitals and $\langle \mu_\alpha | (\mathbf{A} - \omega_L \mathbf{A})^{-1} |$ describes the first-order change in the ground state molecular orbitals due to the electric-dipole perturbation. Explicit expressions for \mathbf{A} and \mathbf{A} are provided, for example, in Ref. [67].

In order to get the \mathbf{A} tensor components, it was necessary to implement the evaluation of the matrix elements corresponding to the electric-quadrupole operator in the basis of unperturbed Kohn–Sham molecular orbitals and to calculate

$$A_{\alpha,\beta\gamma} = \langle \mu_\alpha | (\mathbf{A} - \omega_L \mathbf{A})^{-1} | \theta_{\beta\gamma} \rangle. \quad (30)$$

SNF acts as meta-program. It collects energy gradients and polarizability tensor values provided by TURBOMOLE and evaluates the normal modes and ROA intensity differences, which are obtained by a direct numerical differentiation of the property tensors with respect to the normal modes. A 3-point central differences formula has been applied, the step length has been set to 0.01 bohr. The energy gradients (needed for the harmonic force field) have been calculated with the BP86 density functional and Ahlrichs' TZVPP basis set [62,68], the polarizability tensors with the density functional BP86 and Ahlrichs' SVP [69], TZVP [62], and TZVPP basis sets. Due to the lack of the TZVPP basis set for the rhodium atom, a TZVP basis set has been used instead. Furthermore, we employed the SVPP basis set, which is the SVP basis set but with the polarization functions taken from Ref. [68]. In addition, calculations of the TZVP basis set have been performed with Becke's three-parameter hybrid-exchange functional B3LYP [70,71]. For all BP86 calculations (except the ones with the SVPP basis set) the resolution-of-the-identity (RI) density-fitting technique as implemented in TURBOMOLE's property module [72,73] could be exploited. Gauge independence of the ROA intensity differences has been assured by employing the velocity representation of the electric-dipole operator for the calculation of the $\beta(\mathbf{G}')^2$ invariant which is available for non-hybrid density functionals.

In order to make sure that no electronic excitation occurs at the wavelength used for the incident light, the corresponding excitation energies have been calculated with TURBOMOLE employing the BP86 density functional in combination with the TZVPP basis set and the B3LYP density functional with the TZVP basis set. For dichloro(sparteine)zinc(II), an excitation wavelength of 488.8 nm was chosen. The spectra of $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III) in Section 4 were also calculated with a laser wavelength of 488.8 nm, because no significant deviations due to (near) resonance were found if the BP86 density functional was employed. The remaining calculations were performed for an excitation wavelength of 799.3 nm, which is far away from any absorption frequency of the cobalt- and rhodium-complexes. The ROA spectra were plotted with a Lorentzian band shape with a full width at half-maximum height of 15 cm⁻¹. Molecular structures and normal modes were visualized using the programs MOLGEN [74] and Jmol [75], respectively.

4. Basis set and density functional dependence

In order to investigate the influence of basis sets and density functionals on ROA spectra of metal complexes, we have performed calculations with the SVP, SVPP, TZVP and TZVPP basis sets and the density functionals BP86 and B3LYP whereby the coordinate and gauge origin has been set to the center of mass in order to keep the gauge origin dependence of the pure length representation as small as possible. We should emphasize that this is the

first study to consider this range of basis set sizes for such large molecules. In addition, we expect to see different results from different density functionals because of the transition metal atoms. All normal modes have been obtained by the BP86 density functional and the TZVPP (for rhodium: TZVP) basis set. We compare the spectra obtained with the $\beta(\mathbf{G}')^2$ invariant and the \mathbf{G}' tensor in the length and velocity representation because the difference between these representations is a measure of the incompleteness and, therefore, of the quality of the basis set (compare Section 2). As an example, the spectra of *A*-tris(acetylacetonato)rhodium(III) are given in Fig. 2.

As expected, the spectra obtained with the distinct representations become the more similar the larger the basis set. This is most obvious for the doublet at 1534/1546 cm^{-1} , which shows a very large absolute intensity difference in the case of the pure length representation and the SVP basis set whereas the corresponding one calculated with $\beta(\mathbf{G}')^2$ in the velocity form has a much smaller value. However, if the

basis set is changed to TZVP and TZVPP, the absolute intensity differences increase with the size of the basis set and are almost the same in magnitude as the ones from the pure length representation. Hence, in the case of *A*-tris(acetylacetonato)rhodium(III), at least the TZVP basis set should be employed for a qualitative picture of the spectra. In order to have a more accurate description of the intensity differences, the TZVPP basis set is needed. Compared to the TZVP and SVP basis sets, it provides more polarization functions, which have already been proven to be important for ROA intensity differences [76]. Interestingly, the spectra obtained in the length representation show very small changes when going from the SVP to the TZVP and TZVPP basis sets which is also an indication for negligible gauge origin dependence. In contrast to that, the spectra which use the $\beta(\mathbf{G}')^2$ invariant calculated in the velocity form, change remarkably. This shows the slower basis set convergence of the velocity representation.

The B3LYP spectrum has been calculated with the TZVP basis set and is only available for the pure length

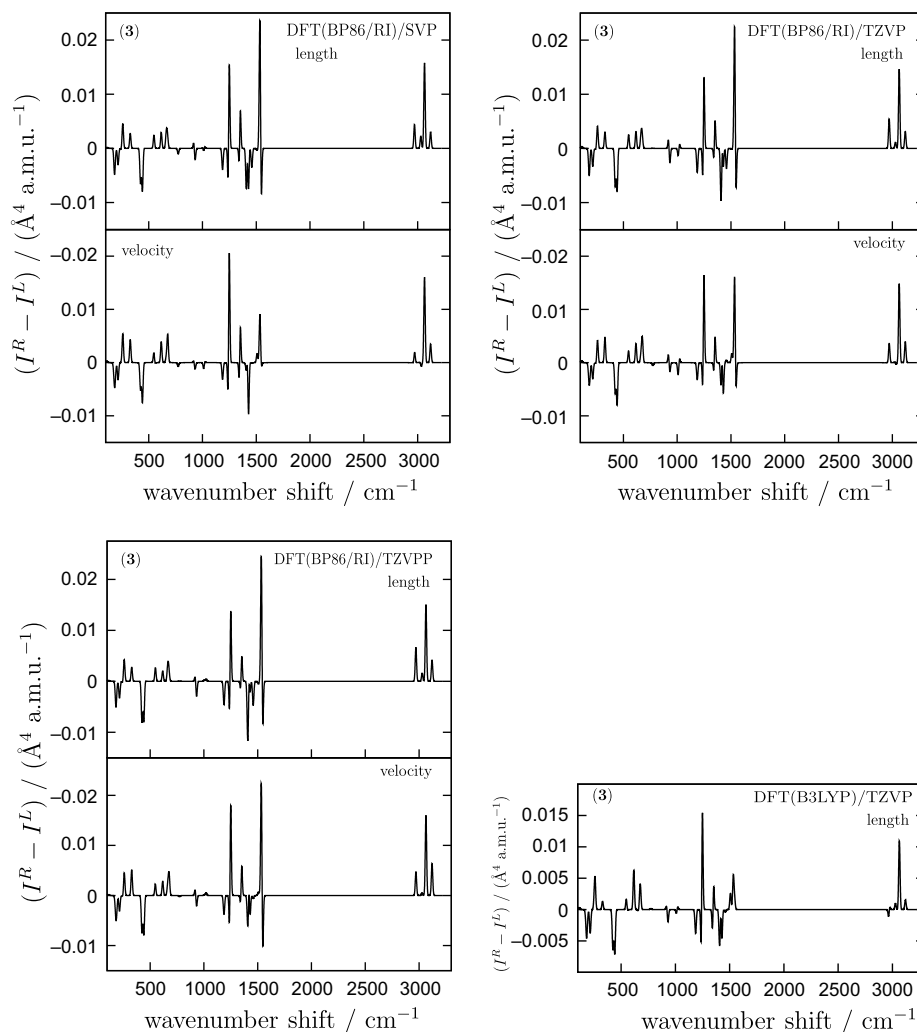


Fig. 2. Calculated ROA spectra (backscattering direction) of *A*-tris(acetylacetonato)rhodium(III) (3) obtained with the density functional BP86 and the SVP, TZVP and TZVPP basis sets and the B3LYP density functional in combination with the TZVP basis set. “length” and “velocity” indicate that the $\beta(\mathbf{G}')^2$ values have been calculated in the length and velocity representation, respectively.

representation. The signs of the intensity differences are quite well reproduced. However, the absolute intensity difference values show noticeable differences when compared to the ones obtained with the BP86 density functional. The error induced by the RI approximation in the calculations employing the non-hybrid density functional is usually negligible (for, e.g. optical rotation less than 2% [73]) and hence, this might not be the reason for such a distinct behaviour. Significant deviations have also been observed between the spectra obtained with the BP86 and B3LYP density functionals for Δ -tris(acetylacetonato)cobalt(III) and $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III), but we have detected negligible deviations for dichloro(sparteine)-zinc(II). This is an indication for the well-known fact that present-day density functionals face difficulties when transition metal atoms are involved. Only Zn as a late transition metal atom is different in this respect and the results obtained for the Zn complex are in agreement with those obtained for organic molecules [30].

We have compared the values of the α , G' and A tensors obtained by BP86 and B3LYP for Δ -tris(acetylacetonato)rhodium(III) and found non-negligible deviations. It has already been observed in optical rotation calculations that the values obtained with the hybrid density functional B3LYP differ from the ones obtained from non-hybrid density functionals. It was assumed that this is due to the fact that excitation energies of valence states are underestimated by B3LYP [77,78]. However, the derivatives of the tensors with respect to the normal modes are necessary for the ROA invariants, not the tensor values alone. Therefore, it is possible that the differences in the tensor values obtained by BP86 and B3LYP vanish upon differentiation. However, this is not found and the differences do not cancel due to the differentiation.

In order to demonstrate the importance of polarization functions for ROA calculations, we have calculated the spectra of $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III) for the SVP, SVPP, TZVP and TZVPP basis sets (see Fig. 3).

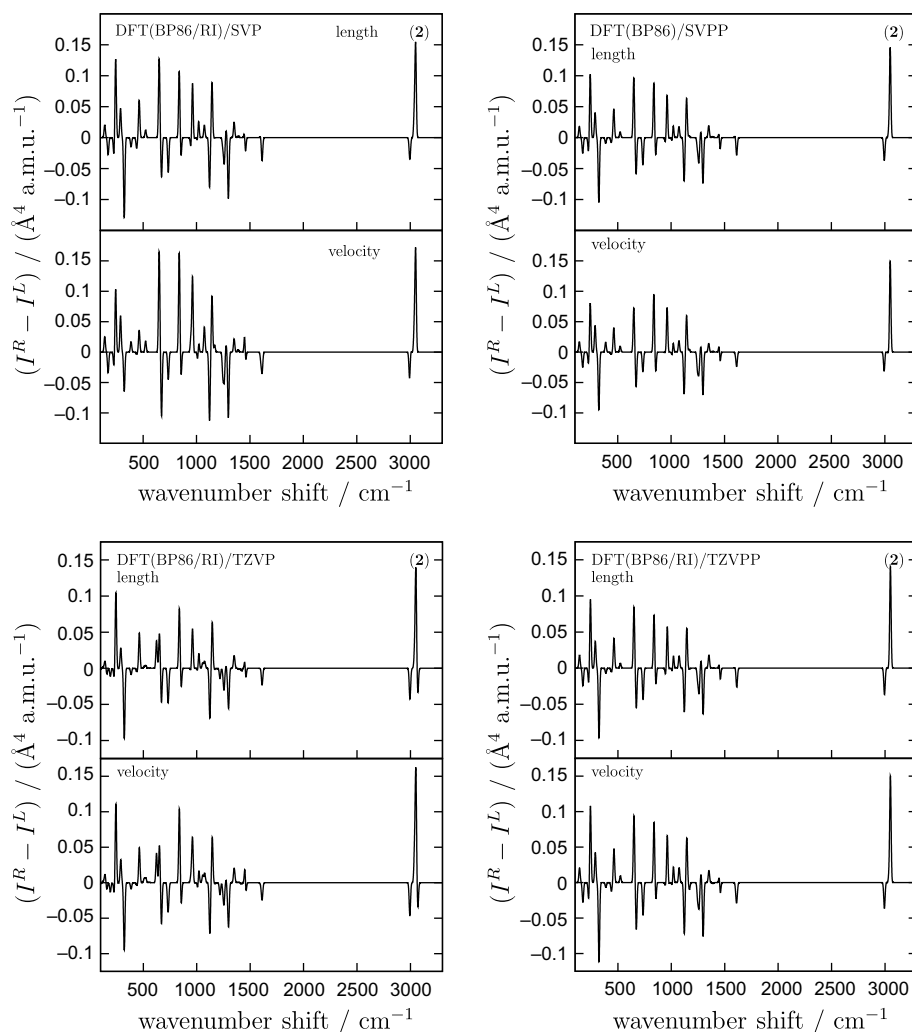


Fig. 3. Calculated ROA spectra (backscattering direction) of $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III) (2) obtained with the density functional BP86 and the SVP, SVPP, TZVP and TZVPP basis sets. “length” and “velocity” indicate that the G' tensor values have been calculated in the length and velocity representation, respectively.

The limit of a complete basis set is more or less reached with the TZVPP basis set since the differences between the spectra obtained with the \mathbf{G}' tensor in the length and velocity form vanish. It is obvious that basis set convergence is faster in the case of the length representation. The role of polarization functions becomes apparent in the comparison between the spectra from calculations with the SVPP and TZVPP basis sets and the ones obtained with the SVP and TZVP basis sets. The spectrum of the pure length form maintained by the SVPP basis set is already very similar to the one from the triple-zeta valence TZVPP basis set although the first one is only a single valence basis set. However, the SVPP basis set contains the same polarization functions as the TZVPP basis set which leads to the high similarity of both spectra for the pure length representation. In contrast to this, the spectra calculated with the \mathbf{G}' tensor in the velocity representation and the SVPP basis set do not resemble the spectra obtained with the TZVPP basis set to such a large extent because of the slower basis set convergence of the velocity form.

5. Results and discussion

The spectra of the cobalt complexes are shown in Fig. 4. The spectrum of Δ -tris(acetylacetonato)cobalt(III) is quite sparse. In the region from 150 to 425 cm^{-1} , deformational (bending, rocking, twist) vibrations of the oxygen atoms occur, whereas the Co–O stretching modes exist at 612 and 643 cm^{-1} . The largest bands of the spectra at 1253 and 1258 cm^{-1} correspond to symmetric and antisymmetric combinations of symmetric C–C stretching vibrations. At 1541 cm^{-1} , a C–O stretching vibration can be found where two ligands show an in-phase symmetric stretching vibration, the third ligand being out-of-phase (compare Fig. 5). The totally in-phase combination occurs at 1554 cm^{-1} . At higher wavenumbers, C–H stretching modes occur in different combinations of (anti)symmetric vibrations of the CH_3 and C–H groups.

In the case of $\Delta(\delta\delta\delta)$ -tris(ethylendiaminato)cobalt(III), the wavenumber region from around 200–1300 cm^{-1} provides a lot of characteristic peaks, whereas between 2900

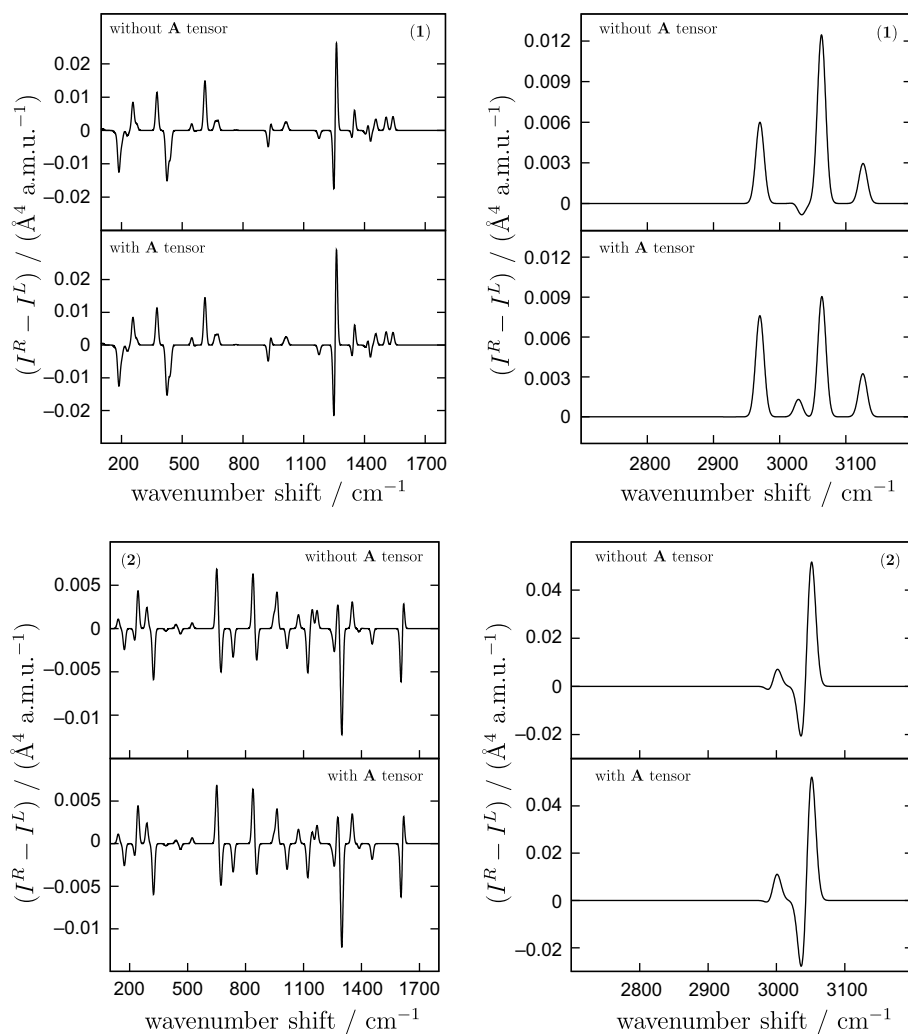


Fig. 4. Calculated ROA spectra (backscattering direction) of Δ -tris(acetylacetonato)cobalt(III) (1) (top) and $\Delta(\delta\delta\delta)$ -tris(ethylendiaminato)cobalt(III) (2) (bottom) obtained with the density functional BP86 and the TZVPP basis set. The upper part of each spectrum shows the plot without the \mathbf{A} tensor contribution, the lower panel provides the full reference spectrum.

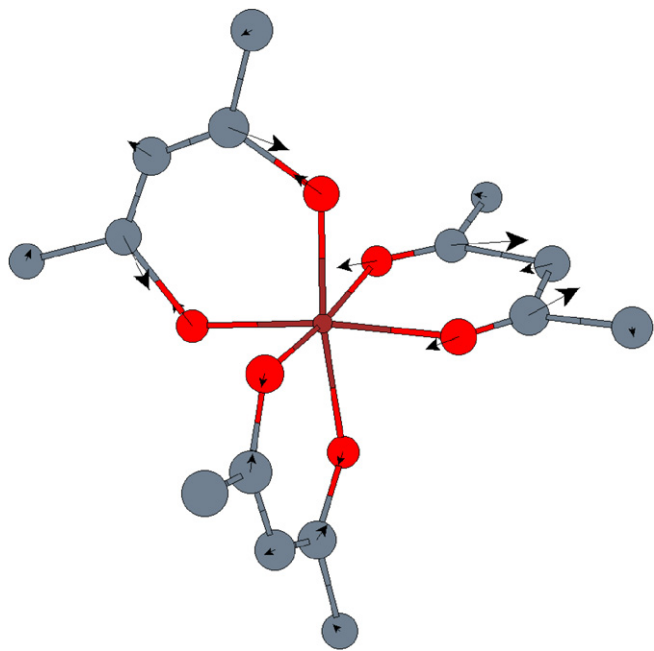


Fig. 5. Vector representation of the normal mode of Δ -tris(acetylacetonato)cobalt(III) (1) at 1541 cm^{-1} .

and 3200 cm^{-1} only three bands of C–H stretching vibrations (symmetric and antisymmetric vibrations in distinct combinations) can be found. The N–H stretching vibrations show up at higher wavenumbers. Deformational vibrations of the nitrogen atoms occur for example at 243 cm^{-1} and stretching vibrations at 324 cm^{-1} . N–H₂ rocking modes give rise to the bands at 651 and 673 cm^{-1} , C–H₂ rocking modes to the peak at 839 cm^{-1} . At 1015 and 1122 cm^{-1} , C–C stretching and C–H₂ rocking vibrations occur. The large negative intensity difference at 1298 cm^{-1} belongs to a twist mode delocalized over the C–H₂ and N–H₂ groups. The doublet at $1606/1614\text{ cm}^{-1}$ corresponds to N–H₂ bending modes. Comparing the spectra of the two cobalt complexes, no significant similarity exists.

The spectra of Δ -tris(acetylacetonato)rhodium(III) and dichloro(sparteine)zinc(II) are given in Fig. 6. Comparing the spectra of the first with the ones of the cobalt analogon, similar intensity differences in the region from 2900 to 3200 cm^{-1} can be found, but very different intensity differences in the region from 100 to 1800 cm^{-1} occur. The wavenumbers, however, deviate not much from the ones obtained for Δ -tris(acetylacetonato)cobalt(III). Therefore, the normal modes of Δ -tris(acetylacetonato)rhodium(III) occur at similar wavenumbers like the ones of Δ -tris(acetylacetonato)cobalt(III). Worth mentioning is the doublet at $1244/1246\text{ cm}^{-1}$, which corresponds to the symmetric and antisymmetric combination of symmetric C–C stretching modes. These modes show the largest absolute intensity differences in the spectra of Δ -tris(acetylacetonato)cobalt(III). In contrast to this, the largest peak in the Δ -tris(acetylacetonato)rhodium(III) spectra is found at 1534 cm^{-1} , which belongs to the already mentioned out-of-phase combination of C–O stretching modes of the ligands, the negative band

at 1546 cm^{-1} belonging to the in-phase combination. These two modes feature much smaller intensity differences in the case of Δ -tris(acetylacetonato)cobalt(III), but the out-of-phase motion appears also at lower wavenumbers than the in-phase combination. Interestingly, the same has been encountered by Sato et al. [31] for the VCD-active C–O stretching vibrations of the open-shell complexes Δ -tris(acetylacetonato)chromium(III) and Δ -tris(acetylacetonato)rhodium(III), whereas they found a reversed order of the C–O stretching vibrations for the closed-shell complexes Δ -tris(acetylacetonato)cobalt(III) and Δ -tris(acetylacetonato)rhodium(III). Therefore, they rationalized that for these closed-shell complexes the in-phase combination is more stabilized by “the symmetric distribution of *d*-electron densities” than the out-of-phase motion.

The spectra of dichloro(sparteine)zinc(II) feature many signals, the ones with the largest absolute intensity differences occurring at about 800 – 1400 cm^{-1} . Compared to $\Delta(\delta\delta\delta)$ -tris(ethylenediaminato)cobalt(III), where the Co–N stretching vibration arises at 324 cm^{-1} , the one of Zn–N emerges at 306 cm^{-1} . N–C stretching vibrations appear, e.g. at 1022 cm^{-1} , deformational vibrations of the hydrogen atoms from 1039 to 1434 cm^{-1} , followed by the C–H stretching vibrations in the wavenumber region from 2800 to 3100 cm^{-1} .

As one can see on the basis of the presented spectra, ROA experiments would be a reliable tool for studying the stereochemistry of chiral metal complexes. Since the spectra of the Δ -tris(acetylacetonato)rhodium(III) and Δ -tris(acetylacetonato)cobalt(III) complexes show significant differences despite the same ligand structure it is to expect that ROA measurements will be sensitive to the metal atoms employed.

5.1. Magnitude of the electric-dipole–electric-quadrupole contribution

There has been some discussion in the literature about the importance of the electric-dipole–electric-quadrupole tensor for ROA intensity differences (for examples, see the references cited in Ref. [79]). Calculations without the *A* tensor contribution were performed by Zuber et al. [26] and recently by us to examine the contribution of the *A* tensor for a test set of organic molecules [79]. It has been found to be small for most vibrations, except for C–H stretching vibrations where the contribution can be very large. Now the question arises if the same holds for ROA spectra of metal complexes, i.e., for a completely different type of molecules. In order to investigate this, we have plotted the spectra with and without *A* tensor contribution in Figs. 4 and 6. For all four molecules, similar patterns can be recognized: in the wavenumber region below 2500 cm^{-1} , no noteworthy difference between the spectrum with and without the $\beta(A)^2$ calculation appears, the *A* tensor contribution is negligible. At higher wavenumbers, some remarkable deviations in the intensity differences exist. An inversion of the sign of a peak, visible at

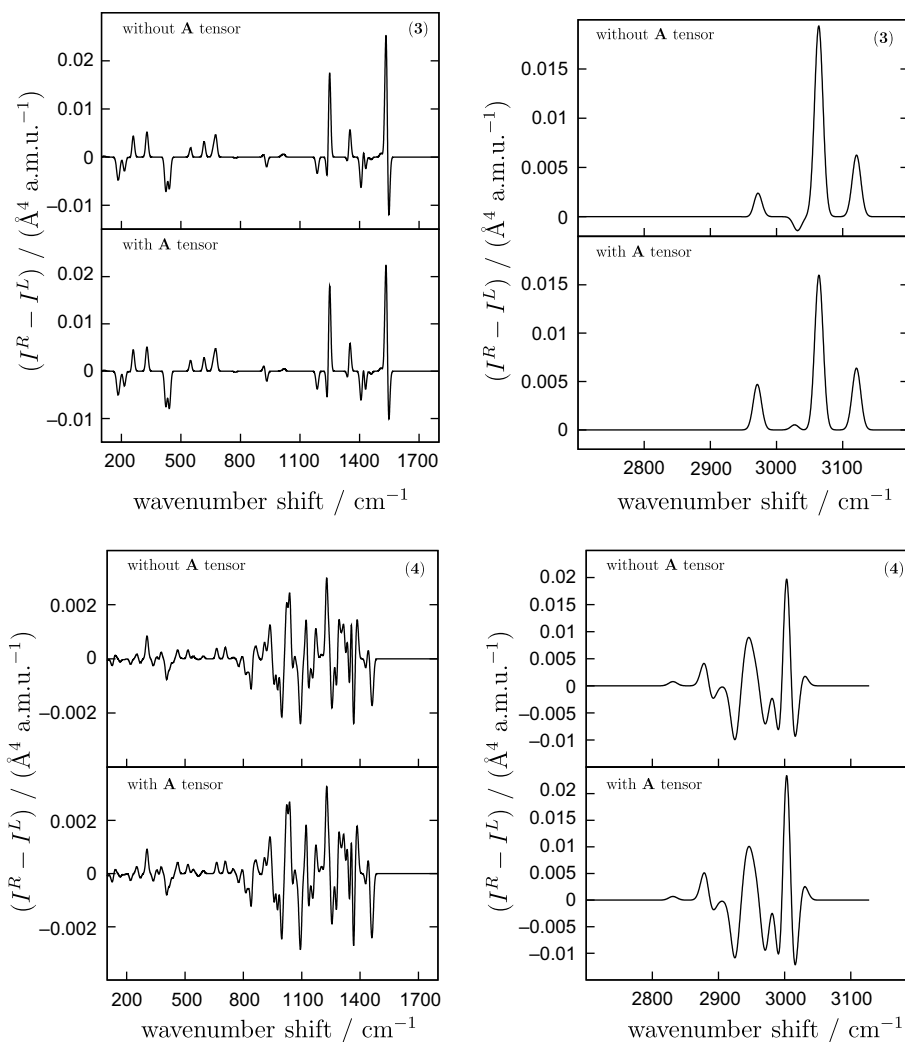


Fig. 6. Calculated ROA spectra (backscattering direction) of *A*-tris(acetylacetonato)rhodium(III) (3) (top) and dichloro(sparteine)zinc(II) (4) (bottom) obtained with the density functional BP86 and the TZVPP basis set. The upper part of each spectrum shows the plot without the *A* tensor contribution, the lower panel provides the full reference spectrum.

3031 cm^{-1} , exists in the spectra of *A*-tris(acetylacetonato)-rhodium(III) and *A*-tris(acetylacetonato)cobalt(III). This band is a superposition of several peaks. It should be noted that no sign inversion can be found for a single intensity difference if one compares the intensity difference values for each peak of this band obtained with and without *A* tensor contribution. The overall differences due to neglect of the $\beta(A)^2$ values are small and do not lead to such remarkable sign inversions of the peaks belonging to C–H stretching vibrations like it has been found for organic molecules [79]. As a consequence, the omittance of the *A* tensor contribution would not lead to a significant change of the spectrum.

6. Conclusion

In this work, we have presented a semi-numerical density-fitting-based implementation for the calculation of ROA spectra of large molecules. With this set-up, it is now possible to routinely obtain consistent force fields

and ROA spectra of large molecules with large basis sets for the first time. Gauge origin independence has been assured by calculating $\beta(G')^2$ in the velocity representation of the electric-dipole operator.

It has been found that the electric-dipole–electric-quadrupole contribution is very small for the four investigated metal complexes, especially at wavenumbers less than 2900 cm^{-1} which is in accordance with results recently obtained for organic molecules [79]. The inclusion of polarization functions has been important for the ROA calculations of the four metal complexes studied. In order to reach the limit of a complete basis set, at least a basis set of TZVPP quality is necessary. Employing the velocity representation of the electric-dipole operator has led to a slower basis set convergence compared to the one of the length form. The density functionals BP86 and B3LYP have yielded distinct intensity differences for the cobalt- and rhodium-complexes. For a final assessment of the density functionals and basis sets and the validation of the approximations made in the calculations, experimental data are

needed. Then, also the necessity of considering, e.g. (near) resonance and solvent effects can be analyzed, which would be another step forward for the theoretical spectroscopy of chiral molecules [80].

Acknowledgement

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Appendix. The $\beta(\mathbf{G}')^2$ invariant at the origin \mathbf{O} is given as (for the sake of clarity, the indication of the origin dependence of all tensor components is omitted in the following)

$$\begin{aligned}\beta(\mathbf{G}')^2(\mathbf{O}) &= \frac{1}{2}(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta}) \\ &= \frac{1}{2}\left[(\alpha_{xx} - \alpha_{yy})(G'_{xx} - G'_{yy}) + (\alpha_{xx} - \alpha_{zz}) \right. \\ &\quad \times (G'_{xx} - G'_{zz}) + (\alpha_{yy} - \alpha_{zz})(G'_{yy} - G'_{zz}) \\ &\quad + 3(\alpha_{xy}(G'_{xy} + G'_{yx}) + \alpha_{xz}(G'_{xz} + G'_{zx}) \\ &\quad \left. + \alpha_{yz}(G'_{yz} + G'_{zy}))\right].\end{aligned}\quad (31)$$

Employing the intuitive notation $(a \times \alpha^p)_{\beta} \equiv \epsilon_{\beta\gamma\delta}a_{\gamma}\alpha^p_{\delta}$, inserting the origin shift of \mathbf{G}' given in Eq. (25) and considering that $\alpha_{\alpha\beta} = \alpha_{\beta\alpha} \forall \alpha \neq \beta$, one obtains for $\beta(\mathbf{G}')^2$ at the shifted origin $\mathbf{O} + \mathbf{a}$ in the velocity form

$$\begin{aligned}\beta(\mathbf{G}')^2(\mathbf{O} + \mathbf{a}) &= \frac{1}{2}\left[(\alpha^p_{xx} - \alpha^p_{yy})\left(G'^p_{xx} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_x \right. \right. \\ &\quad \left. \left. - G'^p_{yy} - \frac{1}{2}\omega_L(a \times \alpha^p_y)_y\right) \right. \\ &\quad + (\alpha^p_{xx} - \alpha^p_{zz})\left(G'^p_{xx} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_x - G'^p_{zz} \right. \\ &\quad \left. - \frac{1}{2}\omega_L(a \times \alpha^p_z)_z\right) + (\alpha^p_{yy} - \alpha^p_{zz}) \\ &\quad \times \left(G'^p_{yy} + \frac{1}{2}\omega_L(a \times \alpha^p_y)_y \right. \\ &\quad \left. - G'^p_{zz} - \frac{1}{2}\omega_L(a \times \alpha^p_z)_z\right) \\ &\quad + 3\left(\alpha^p_{xy}\left(G'^p_{xy} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_y \right. \right. \\ &\quad \left. \left. + G'^p_{yx} + \frac{1}{2}\omega_L(a \times \alpha^p_y)_x\right) \right. \\ &\quad + \alpha^p_{xz}\left(G'^p_{xz} + \frac{1}{2}\omega_L(a \times \alpha^p_x)_z + G'^p_{zx} \right. \\ &\quad \left. + \frac{1}{2}\omega_L(a \times \alpha^p_z)_x\right) + \alpha^p_{yz}\left(G'^p_{yz} + \frac{1}{2}\omega_L(a \times \alpha^p_y)_z \right. \\ &\quad \left. \left. + G'^p_{zy} + \frac{1}{2}\omega_L(a \times \alpha^p_z)_y\right)\right) \\ &= \beta(\mathbf{G}')^2(\mathbf{O}) + \frac{1}{2}\omega_L\left[\alpha^p_{xx}(a_y\alpha^p_{xz} - a_z\alpha^p_{xy}) \right. \\ &\quad \left. - \alpha^p_{xx}(a_z\alpha^p_{yx} - a_x\alpha^p_{yz}) - \alpha^p_{yy}(a_y\alpha^p_{xz} - a_z\alpha^p_{xy}) \right. \\ &\quad \left. + \alpha^p_{yy}(a_z\alpha^p_{yx} - a_x\alpha^p_{yz}) + \alpha^p_{xx}(a_y\alpha^p_{xz} - a_z\alpha^p_{xy}) \right. \\ &\quad \left. - \alpha^p_{xx}(a_z\alpha^p_{yx} - a_x\alpha^p_{yz}) - \alpha^p_{yy}(a_y\alpha^p_{xz} - a_z\alpha^p_{xy}) \right. \\ &\quad \left. + \alpha^p_{yy}(a_z\alpha^p_{yx} - a_x\alpha^p_{yz}) + \alpha^p_{zz}(a_z\alpha^p_{yx} - a_x\alpha^p_{yz}) \right. \\ &\quad \left. + \alpha^p_{zz}(a_y\alpha^p_{xz} - a_z\alpha^p_{xy}) + \alpha^p_{zz}(a_x\alpha^p_{yz} - a_y\alpha^p_{zx}) \right. \\ &\quad \left. + \alpha^p_{yz}(a_z\alpha^p_{zx} - a_x\alpha^p_{zz})\right] = \beta(\mathbf{G}')^2(\mathbf{O}).\end{aligned}$$

As one can see, the gauge dependence vanishes because the additional terms which arise due to the gauge dependence of \mathbf{G}'^p cancel each other.

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