Circular Dichroism Spectrum of [Co(en)$_3$]$^{3+}$ in Water: A Discrete Solvent Reaction Field Study

L. JENSEN,1 MARCEL SWART,2 PIET TH. VAN DUIJNEN,3 J. AUTSCHBACH4

1Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA
2Theoretical Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
3Theoretical Chemistry, Materials Science Centre, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
4Department of Chemistry, State University of New York at Buffalo, 312 Natural Science Complex, Buffalo, New York 14260-3000, USA

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ABSTRACT: In this work we investigate the circular dichroism (CD) spectrum of [Co(en)$_3$]$^{3+}$ in water, using the discrete solvent reaction field (DRF) model. The DRF model is a polarizable quantum mechanics/molecular mechanics (QM/MM) model. The implementation of the DRF model for CD spectra calculations based on time-dependent density functional theory (TDDFT) is presented. The combination of DRF with TDDFT allows for a computationally attractive solution for calculating chiroptical properties of molecules in solution when explicit solvent structures are of interest. Using a mixed coarse/fine-grained parallel computation, we show that average CD spectra from snapshots of the solvent structure can be obtained routinely. Classical polarizable molecular dynamics (MD) simulations have been used to obtain the solvent structure around the [Co(en)$_3$]$^{3+}$ (en = ethyldiamine) solute. We show that the final spectrum converges quickly with respect to the number of configurations. The DRF results were compared with results obtained from the much simpler conductor-like screening model (COSMO). Both models predicted similar blue shifts of the CD bands, but none of the...
1. Introduction

Considering the chemical environment of a molecule is an important task when calculating its spectral and other properties. For instance, because many measurements are carried out in solution, the solvent–solute interactions must be modeled computationally. Conceptually the easiest approach in a quantum mechanical framework is to include solvent molecules explicitly in the calculation (i.e., a supermolecule is calculated). If the supermolecule is further considered in a molecular dynamical (MD) simulation, the property of interest can be calculated as the system evolves in time. This often represents a highly accurate treatment of the system, since all possible interactions between solute and solvent are considered on the same quantum mechanical footing. However, the supermolecule approach is not generally feasible computationally. The computational cost problem might be amplified in calculations of molecular properties as compared with ground-state energies and gradients either because the property is intrinsically more expensive to calculate or because of the lack of highly optimized implementations. Besides the computational cost, a problem with this type of model is that there is no unique way of defining properties of the individual molecules [1–3]. This can be particular problematic when considering response properties [2, 4–7].

When studying the spectroscopic properties of molecules, solvent effects can often be considered as comparatively small perturbations of the molecule of interest. Thus, it is desirable to devise solvent models that capture the essence of these effects without introducing additional electronic degrees of freedom that have to be treated quantum mechanically. Polarizable continuum models (PCMs) have been quite successful in this respect [8–10]. One disadvantage of PCMs, however, is that the solvent–solute interaction is rather nonspecific and considers neither the molecular structure of the solvent nor a possible structural framework of the solvent such as the hydrogen–bond network in water.

The explicit structure of the solvent is straightforwardly included in the combined quantum mechanics/molecular mechanics (QM/MM) methods [11–22]. As in the continuum model, the solute is separated from the solvent molecules and the molecular properties of the solute are therefore well defined. The discrete representation of the solvent molecules introduces a large number of solvent configurations over which the solute properties must be averaged. This is typically done using Monte Carlo or MD techniques, which lead to a large number of quantum mechanical calculations to be carried out. For this reason, a combination of density function theory (DFT) and MM models is of particular interest.

We have developed a polarizable QM/MM model within DFT to study the molecular response properties in solution [23–26]. This discrete solvent reaction field (DRF) model combines a DFT description of the solute molecule with a classical description of the discrete solvent molecules. The latter are represented using distributed atomic charges and polarizabilities. The advantages of including polarizabilities in the MM part is that all parameters can be obtained from gas-phase properties. The permanent point charges represent at least the permanent molecular dipole moment, and the distributed atomic polarizabilities the full molecular polarizability tensor. The atomic charges are straightforwardly obtained using multipole derived charges (MDC) [27] and the distributed polarizabilities by adopting standard parameters or refitting them to match the calculated polarizability tensor [28–31]. This allows for a simple procedure to obtained the solvent model parameters which subsequently can be used in the MD and QM/MM simulations. This model has been used successfully to study response properties of molecules in solution due to an electric field in particular nonlinear optical properties.

Solvent effects on chiroptical properties have been previously considered in calculations based on continuum models. For example, Mennucci et al. [32] have studied the optical rotation of organic molecules in solution by DFT. Recently,
Pecul et al. [33] have investigated solvent effects on circular dichroism (CD) spectra, also with DFT. It was found that some improvement can be obtained with continuum models, although the results indicated that quantitative agreement with experimental data is likely to require a more sophisticated treatment of the solvent–solute interaction.

In our previous work on the CD of transition metal complexes [34], the conductor-like screening model [35, 36] (COSMO), also of the continuum model type, was applied in an approximate way in DFT calculations. Large solvent effects were obtained for the energy and intensity of charge-transfer (CT) excitations in ML₃ systems, where M is a metal ion tri-cation and L a neutral bidentate ligand. The solvent was water. For systems with charge smaller than +3 or less polar solvents, the effect was found to be much less pronounced, though still noticeable [34, 37]. In these calculations, only the solvation of the ground state was considered, and not the dynamic response of the solvent due to the perturbing electric field. We argued in Ref. [34] and subsequent publications [37–39] that because of the high dielectric constant and polarity of water, this should represent a good approximation [9]. Part of the present work will be devoted to demonstrating that this is indeed the case. The largest solvent effect was found for [Co(tn)₃]³⁺, where the main CT band in the CD spectrum was blue-shifted by >6 · 10⁹ cm⁻¹ upon incorporation of the continuum model in the calculations. A slightly less strong effect was found for the complex [Co(en)₂]³⁺. In both cases, the agreement with experiment was significantly improved.

In the present work, we investigate the solvent effects on the CD spectrum of Λ-[Co(en)₃]³⁺ with the DRF solvent model, including the dynamic polarization of the solvent. The complex [Co(en)₂]³⁺ was chosen for two reasons. First, it represents a very well-studied “benchmark” system both theoretically and experimentally [40]. Second, we found previously that the CD spectrum is not strongly dependent on the conformation of the chelate rings (which are usually classified as ob and lel, depending on whether the plane of the ring is oblique or parallel to the C₃ symmetry axis of the complex [40]). Solvent effects on the CD spectrum of [Co(tn)₃]³⁺ were found to be somewhat larger than for [Co(en)₂]³⁺ in our previous computations. However, for [Co(tn)₃]³⁺, we also showed that the shape of the CD spectrum, in particular in the low-energy region, critically depends on the chelate ring conformation. The focus of this study is on the solvent effects and a comparison of the DRF with the COSMO continuum model. Conformational changes would introduce an additional layer of complexity; therefore [Co(en)₂]³⁺ is the preferred system to study. Apart from evaluating the performance of the DRF model for this type of calculation, our goal was to verify that neglecting the response of the solvent as done in previous calculations represents an excellent approximation.

This work is organized as follows. The implementation of the DRF model in the framework of CD spectra calculations based on time-dependent DFT (TDDFT) is described in Section 2. Computational details are outlined in Section 3. The results for [Co(en)₂]³⁺ are presented and discussed in Section 4. Section 5 presents some concluding remarks and an outlook.

2. Theory

In the DRF model, the QM/MM operator at a point rᵢ is given by [23–26]:

\[ \hat{H}_{\text{QM/MM}} = \sum_i \hat{H}^{\text{DRF}}(r_i, \omega) \]

\[ = \sum_i \hat{H}^{el}(r_i) + \sum_i \hat{H}^{\text{pol}}(r_i, \omega) \]

\[ = \sum_i \frac{q_i}{R_{is}} + \sum_{i,s} \mu_{s,i}^{\text{ind}}(\omega) \frac{R_{s,i}}{R_{is}^2}, \]

(1)

where the first term, \( \hat{H}^{el} \), is the electrostatic operator, which describes the Coulomb interaction between the QM system (the solute) and the permanent charge distribution of the solvent molecules. The second term, \( \hat{H}^{\text{pol}} \), is the polarization operator, which describes the many-body polarization of the solvent molecules.

The induced atomic dipole at a site \( s \) is given by

\[ \mu_{s,i}^{\text{ind}}(\omega) = \alpha_{s,\alpha} \left[ F^{\text{init}}_{s,\beta}(\omega) + \sum_{i,p} \tau_{p,i}^{(2)} \mu_{i,p}^{\text{ind}}(\omega) \right], \]

(2)

where \( \alpha_{s,\alpha} = \delta_{s,\alpha} \alpha_\alpha \) is a component of the polarizability tensor of an isotropic atom at site \( s \), and \( \tau_{p,i}^{(2)} \) is the screened dipole interaction tensor [23, 28, 29]. We assume that the atomic polarizabilities are independent of the frequency, but the model can easily be extended to include this effect as well [30, 31]. \( F^{\text{init}}_{s,\beta}(\omega) \) is the initial electric field at site \( s \) and consists of the field arising from the frequency-dependent electronic charge distribution of the QM part, the
field from the QM nuclei, and the field from the point charges at the solvent molecules.

The DRF operator is combined with the time-dependent Kohn–Sham (TD-KS) equations and linear response theory to obtain a perturbative solution to the TD-KS equations [41–45]. The first-order change in the density due to a frequency-dependent perturbation, \( \rho^\prime(r, \omega) \), is given by

\[
\rho^\prime(r, \omega) = \sum_{s,t} P'_{st}(\omega) \varphi_s(r) \varphi^*_t(r),
\]

where \( P' \) is the first-order density matrix and \( \varphi_s(r) \) the KS orbitals. The first-order density matrix can be expressed in terms of the change in an effective potential, \( V_{\text{eff}} \), by expanding the KS equations to first-order in the perturbing potential as

\[
P'_{st}(\omega) = \frac{n_{is} - n_{it}}{\omega - \omega_{st}} V_{\text{eff}}(\omega),
\]

where \( n_{is} = n_i - n_s \) is the difference in orbital occupations numbers and \( \omega_{st} = \epsilon_s - \epsilon_t \) is the difference in the KS orbital energies. The change in the effective potential depends on the first-order change in the density and is given by

\[
V_{\text{eff}}(\omega) = V_{\text{eff}}(\omega) + \sum_{st} K_{st,\omega} P'_{st}(\omega),
\]

where the coupling matrix, \( K \), has been introduced. The coupling matrix consist of three terms

\[
K_{st,\omega} = K_{st,\omega}^C + K_{st,\omega}^{XC} + K_{st,\omega}^{\text{DRF}},
\]

The first term describes the response of the Coulomb potential, and the second term the response of the exchange-correlation (XC) potential. The last term is specific to the DRF method and yields the respective contribution to the perturbed effective potential. A complete expression for the coupling matrix including the DRF terms can be found in Ref. [24]. Using Eq. (5), Eq. (4) can be written as a set of linear equations where we use the fact that only elements relating occupied \((i,j)\) and virtual \((a,b)\) orbitals are nonzero. These equations can then be expressed in matrix form as the so-called random-phase approximation (RPA) equations. Using the more common notation \( X_{\hat{a}} = P_{\hat{a}} \) and \( Y_{\hat{b}} = P_{\hat{b}} \), one obtains

\[
\begin{bmatrix}
    A & B \\
    B^* & A^*
\end{bmatrix}
\begin{bmatrix}
    -1 & 0 \\
    0 & 1
\end{bmatrix}
\begin{bmatrix}
    X \\
    Y
\end{bmatrix}
= -\begin{bmatrix}
    V_{\text{eff}} \\
    V_{\text{eff}}^*\end{bmatrix},
\]

where the individually matrix elements are defined as

\[
A_{ij,\hat{a}} = \delta_{ia} \delta_{\hat{a}j} (\epsilon_a - \epsilon_i) + K_{\hat{a},ij}
\]

and

\[
B_{ij,\hat{a}} = K_{ij,\hat{a}}.
\]

Here, it has been assumed that all orbitals have orbital occupations numbers of either 0 or 1, i.e., a closed-shell system. The left-hand side of Eq. (7) can be transformed into a pseudo-eigenvalue equation reading

\[
\Omega F_{00} = \omega^2_{00} F_{00},
\]

where \( \omega_{00} \) is the excitation energy and the Hermitian matrix \( \Omega \) is

\[
\Omega = -S^{-1/2} (A + B) S^{-1/2},
\]

with the diagonal matrix \( S \) given by

\[
S = -(A - B)^{-1}.
\]

From the solutions to the pseudo-eigenvalue problem, the electronic transition dipole moment is obtained as

\[
\langle \lambda | \hat{\mu} | \lambda \rangle = \omega_{00}^{-1/2} D S^{-1/2} F_{00},
\]

where \( D \) is a vector with the occupied-virtual orbital matrix elements of \( \hat{\mu} \), the electric dipole operator. Similarly, the magnetic transition dipole moment is given by

\[
\langle \lambda | \hat{m} | 0 \rangle = -\omega_{00}^{1/2} M S^{1/2} F_{00},
\]

where \( M \) contains the matrix elements of \( \hat{m} \), the magnetic dipole operator.

The rotary strength for the transition \( 0 \to \lambda \) in the length gauge is then straightforwardly given by the well known expressions [46]

\[
R_{0\lambda} = \text{Im} \langle 0 | \hat{\mu} | \lambda \rangle \langle \lambda | \hat{m} | 0 \rangle.
\]

Likewise, the oscillator strength by

\[
f_{0\lambda} = \frac{2}{3} \omega_{00} \text{Re} \langle 0 | \hat{\mu} | \lambda \rangle \langle \lambda | \hat{\mu} | 0 \rangle,
\]

where we simply substitute Eqs. (13) and (14) for the transition dipole matrix elements. The dipole-velocity form of (14) has also been implemented by us, which leads to origin-independent rotary strengths. (For details, see Ref. [47].)
The solute molecule was represented by distributed atomic polarizabilities [29] that were fitted to reproduce the molecular polarizability of 183.8 a.u.; the latter value was obtained from linear response equations within TDDFT using the Becke-Perdew [51, 52] exchange-correlation functional in a triple-ζ valence plus polarization functions (TZP) basis set of Slater-type orbitals (STOs) using the ADF program [53]. The fitted atomic polarizability values are 12.5582 (Co), 3.1325 (N), 0.9240 (H), 16.2170 (C) a.u. [29]. Atomic partial charges for the solute were taken from the MDC analysis [27] (MDC-q charges) that give by construction the best representation of the electrostatic potential outside the molecule, and represent both the atomic and molecular multipoles exactly.

3. Computation Details

3.1. MD SIMULATIONS

The [Co(en)$_3$]$^{3+}$ solute (see Fig. 1) surrounded by 256 water molecules was placed in a spherical box with a radius of 23.9 atomic units (a.u.), and followed during molecular dynamics [48] simulation runs using the DRF90 program [49]. The equilibration run was performed for 25 ps, and the subsequent production run for 25 ps. A soft wall-force potential [49] was used to keep the solvent molecules from evaporating. The simulations were performed at 298 K in the NVT ensemble, using the Verlet scheme [48] and a Nosé-Hoover thermostat [50] to keep the temperature constant. In the production run, every 0.5 ps a snapshot configuration of solvent molecules around the solute was kept for further analysis and the calculation of an averaged CD spectrum (see below). The water molecules were represented with atomic polarizability values of 9.3005 (O) and 0.0690 (H), and atomic charges (qH +0.443, qXX −0.886; the additional point charge XX is placed 0.15 Å from oxygen towards the hydrogens along the HOH-angle-bisecting line) that represent the dipole and quadrupole moment of water. For the van der Waals interaction, a 6–12 Lennard–Jones potential was adopted with parameter taken from Ref. [26].

3.2. CD SPECTRUM

From the MD simulation, 50 snapshot configurations were taken during the production run for a calculation of an averaged DRF CD spectrum (see Fig. 2 for a typical example of a configuration).
Although the total number of configurations is somewhat small, it should still give an accurate average since the configurations are uncorrelated [34]. In the DRF calculations, the atomic polarizability was the same as in the MD simulations, but for technical reasons the point charge was \( q_H = 0.3295 \) and \( q_O = -0.6590 \), which corresponds to the same dipole moment but with the negative charge on the oxygen atom rather than the XX point. For each snapshot configuration, a TDDFT calculation of the lowest 45 excitation energies and their rotational strengths was carried out with the ADF program using the code described in Refs. [55] and [47]. Because of the solvent, the \( D_3 \) symmetry of the complex was not employed. We have used the TZP basis set of the ADF library and the Becke–Perdew GGA functional, along with an integration parameter of 4.5 and a “linear scaling” parameter of 8.0. Atomic orbitals up to \( 2p \) for Co and the 1s shells of C and N were treated as frozen-core orbitals in the computations. Analytic integrals were used for the electric and magnetic dipole moment perturbations. The simulations of the CD spectrum of \([\text{Co(en)}_3]^{3+}\) in the present study were based on origin-independent rotational strengths calculated with the dipole-velocity form of the electric transition dipole moment. All calculations have been carried out for the optimized \( \sigma_b \) conformer of \( \Delta-[\text{Co(en)}_3]^{3+} \) (data taken from Ref. [34]). Rotatory strengths have subsequently been multiply by \( -1 \) for comparison with experimental data for \( \Lambda-\Delta-[\text{Co(en)}_3]^{3+} \). Calculations with the COSMO solvent model applied to the ground state (H\(_2\)O, default radii for atomic spheres [36]) were also performed for comparison with the results of Ref. [34].

It has been found in our previous study of \([\text{Co(en)}_3]^{3+}\) [34] and a number of follow-up studies of \( D_3 \)-symmetric metal complexes [37–39] that within the energy range of the experimentally available CD spectra, only valence excitations are important that do not require diffuse basis functions. Further, it was found that additional polarization functions on the metal do not yield improved results.

The computed rotational strengths for the 45 lowest excitations were transformed into a simulated CD spectrum by applying a Gaussian broadening. An empirical recipe of Mason and coworkers [56] for the linewidth has been employed \((\Delta \tilde{v} = 7.5 \cdot \sqrt{\tilde{v}}, \) with \( \tilde{v} \) in \( \text{cm}^{-1} \)) , which has previously yielded reasonable overall agreement with experimental data for a number of complexes [34], in particular for low-energy transitions. The software for producing a simulated CD spectrum from the ADF (and other quantum chemistry programs) output is available from our group’s web page [57]. The averaged spectrum from the DRF calculations has been obtained from the arithmetic mean of a number \( n \) simulated CD spectra, i.e., after the Gaussian broadening has been applied. A Mathematica notebook designed to perform the spectral averages and to create graphics and animations is available from one of the authors (J. A.) upon request.

The calculation of the CD spectra was performed in a mixed coarse/fine-grained parallel computation. All 50 spectra were calculated simultaneously on a total of 400 processors. We emphasize this procedure since, with the availability of large parallelized commodity-type computer clusters, averaged properties obtained from quantum chemical methods based on geometry snapshots from MD simulations can be obtained within a few hours of turnaround time in a routine fashion.

4. Results and Discussion

For the convenience of the reader, Figure 3 shows the results of our previous calculation on \([\text{Co(en)}_3]^{3+}\) in comparison with experiment. Owing to deficiencies of the applied GGA functional, the calculated \( d-d \) transitions at low energy were too high in energy by \( \sim 6 \cdot 10^3 \text{ cm}^{-1} \). This issue was discussed and analyzed in detail in Ref. [34]. We point out that besides these DFT-specific deficiencies, the qualitative agreement of the calculated and experimental CD spectrum of \( \Lambda-\Delta-[\text{Co(en)}_3]^{3+} \). Results taken from Ref. [34]. Calculated excitation energies and rotational strengths indicated as a “bar spectrum.” For easier comparison with experiment, the lowest calculated pair of transitions was red shifted by \( 6 \cdot 10^3 \text{ cm}^{-1} \). Solvent effects were included via the COSMO continuum model.

**FIGURE 3.** Calculated and experimental CD spectrum of \( \Lambda-\Delta-[\text{Co(en)}_3]^{3+} \). Results taken from Ref. [34]. Calculated excitation energies and rotational strengths indicated as a “bar spectrum.” For easier comparison with experiment, the lowest calculated pair of transitions was red shifted by \( 6 \cdot 10^3 \text{ cm}^{-1} \). Solvent effects were included via the COSMO continuum model.
with experiment is satisfactory and allows an assignment and interpretation of the spectrum. For further details, see Ref. [34] regarding solvent effects and a general assignment of the spectrum, and Ref. [39] for an analysis of the origin of the d-d as well as the CT optical activity in terms of polar and azimuthal distortions of the octahedral ligand field.

Since the d-d region is not significantly affected by the presence of the solvent (H₂O), we focus on the CT region of the spectrum (>35 \cdot 10^3 \text{cm}⁻¹). Accordingly, in other spectra shown here, the low-intensity part of the spectrum is not magnified as in Figure 3. In Figure 4, the results of our DRF calculations are compared with the COSMO model and a calculation without solvent. The DRF result represents an average of 50 individual CD spectra as described in Section 3. First, we draw attention to the COSMO CD spectrum, which is based on rotary strengths calculated in dipole-velocity gauge. It compares well with the spectrum of Figure 3 published previously in Ref. [34], which is based on the dipole-length gauge. In both calculations, the same basis has been used. The agreement validates the suitability of the TZP basis applied here for the purpose of CD spectra calculations in complexes with valence-only transitions.

When comparing the two solution spectra (DRF and COSMO) with the gas-phase spectrum, it is seen that the solvent effects are similar. Both solvent models significantly blue-shift the CD bands above 35 \cdot 10^3 \text{cm}⁻¹. The effect from the COSMO model is stronger; i.e., the blue shift is more pronounced. At the same time, the intensity of the CD is strongly increased in the COSMO calculations, but not as much in the DRF calculations. In comparison with experiment (Fig. 3), the increase in intensity is undesirable. However, the positions of the most intense CT CD bands from the COSMO calculation agree slightly better with experiment than the DRF ones.

The convergence of the DRF spectrum with the number of configurations included in the average is rapid. We used a number \( \Delta \) to assess this convergence. Each simulated “snapshot” CD spectrum \( \kappa \) was calculated in the form of \( \Delta \varepsilon_i^k \) values for 301 energies \( E_i \) between 20 and 60 \cdot 10^3 \text{cm}⁻¹. For \( n = 1 \ldots 50 \), we have then averaged a number of \( n \) spectra to obtain averaged \( \Delta \varepsilon_i^n = \frac{1}{n} \sum_{k=1}^{n} \Delta \varepsilon_i^k \). The convergence value in step \( n, n > 1 \) was then defined as

\[
\Delta(n) = \sum_{i=1}^{301} \left| \Delta \varepsilon_i^n \right| - \left| \Delta \varepsilon_i^{n-1} \right| \quad (17)
\]

[with \( \Delta \varepsilon \) in units of \( 1/(\text{mol cm}) \)]. It should approach zero for large \( n \). Figure 5 displays \( \Delta \) as a function of \( n \) for the DRF CD spectrum of [Co(en)₃]⁺. For \( n > 35 \), we observed very little change in the averaged CD spectrum except for two outliers. There are two main reasons for the modest number of configurations needed to obtain average results. The first reason is that in the MD simulations the water molecules are treated as rigid and [Co(en)₃]⁺ with a fixed structure. This greatly reduces the configuration space and thereby the number of configurations needed. The second reason is that we are interested in simulating the total spectrum and have therefore chosen the convergence criteria given by Eq. [17]. Test calculations did show that changes in the linewidth

![Figure 4](image1.png)

**Figure 4.** Comparison of CD spectrum of \( \Lambda - [\text{Co(en)}_3]^3^+ \) calculated without solvent effects (gas phase), with the COSMO solvent model, and obtained from the average of 50 DRF spectra. See supporting information.

![Figure 5](image2.png)

**Figure 5.** Convergence of the averaging procedure for the CD spectrum of [Co(en)₃]⁺⁺ calculated with the DRF solvent model. For the definition of \( \Delta \), see Eq. 17.
had little effect on the convergence pattern. If we were interested in obtaining absolute values for the individual rotatory strengths accurate to several decimals, one would naturally require many more configurations. Of course, the actual number of configurations needed to obtain average results will depend in general on the property calculated and the system considered.

For smaller $n$, we observed rather large changes in the averaged CD spectrum when increasing $n$ by one. The changes were found mainly in the intensities, but not in the positions of the CD bands. The intensity changes between different configurations were of similar order of magnitude as the differences between the COSMO and the DRF results. Thus, the charge-transfer CD intensity of the [Co(en)$_3$]$^{3+}$ spectrum is quite sensitive to the solvent–solute interaction. This also explains why the COSMO influence is so large. In the DRF MD calculation, each snapshot has a unique, locally anisotropic, solvation shell. This causes a rather similar blue shift of the CT bands in the CD calculations and a high sensitivity in the intensities due to the solvent shell configuration.

A film showing the averaged CD spectrum of [Co(en)$_3$]$^{3+}$ as a function of $n$ is available in the Supporting Information. Further, we provide graphics for the simulated spectrum for each of the 50 configurations of the DRF MD simulation.

An assessment of the overall performance of the solvation models in comparison with experiment is somewhat difficult. On the one hand, the DRF model leads to less intense CT bands, which are therefore in better agreement with experiment. On the other hand, the blue shift of the CT bands is not as large as with the much simpler COSMO model, which leads to slightly less good agreement with the experimental positions of the CT bands. Another problem with the calculations, both COSMO and DRF, is the presence of a weaker pair of CT bands ($\delta/\varepsilon$ in Fig. 3) $\sim 40 \cdot 10^3$ cm$^{-1}$ that is not visible in the experiment. As discussed in Ref. [34], it might be that the splitting between the $\delta$ and $\varepsilon$ band is overestimated in the calculations; otherwise, there would be a cancellation of the Cotton effects. Another possibility is that the energies of this pair of CD bands are very sensitive to the solvent configuration, and thus a MD averaging procedure would have led to their disappearance. The fact that the DRF calculations predicts a lowering of these bands indicates that this might be true to some extent. However, the effect is not strong enough to cancel the Cotton effects. A third possibility, which remains to be investigated, is whether deficiencies in the XC potential and kernel cause these two particular transitions to occur at much too low energy.

Regarding the overestimation of the CD intensity at high excitation energies, because empirical linewidths are applied in the spectra simulations it is, of course, possible to choose them in order to reproduce the intensities correctly. However, when applying a uniform Gaussian broadening, only the low- or the high-energy part of the spectrum can be reproduced well. The empirical recipe by Mason and coworkers [56] that was applied here assumes that the linewidth increases with $\sqrt{E}$, the square root of the excitation energy. This behavior accounts for the decreased lifetime of higher-lying states, and perhaps as well for a decreasing experimental sensitivity at high energies. Mason’s recipe yields good agreement between theory and experiment for the low-energy part of the spectrum, but at high energies the calculated intensities are still too high. A reduction in intensity and a further broadening of the bands would be obtained by assuming that the linewidth increases faster than $\sqrt{E}$. We have decided not to investigate this issue further, since at present it is not clear how various approximations in the calculation might affect the linewidths at high energy. It is not unlikely that too high intensities are caused by the neglect of vibronic coupling in the calculations [58].

One aspect in which the DRF and COSMO approaches as applied here differ is that the COSMO calculations did not consider the dynamic response from the solvent. An implementation that will consider these effects in COSMO calculations with ADF is currently under way in our group. The approximation can be considered as a nonequilibrium solvation model where the fast (optical) part of the dielectric constant is one. This is a fair approximation for many solvents, since the optical dielectric constant is in general between 1.5 and 2.0. To confirm that the differences between DRF and COSMO are not caused by this approximation, we have performed additional DRF CD calculations on [Co(en)$_3$]$^{3+}$ for the same 50 MD snapshots configurations, but neglecting the response of the dynamic solvent. Figure 6 displays the averaged spectra (50 configurations) for both cases. Indeed, the two spectra are virtually indistinguishable, showing that for the intended type of application (highly charged metal complex in a polar solvent), the majority of the solvent effect on the CD spectrum is simply due to the solvation of the ground state, and a negligible contribution from the dynamic solvent response. Since the approximation leads to a significant reduction in computational time, it is desirable to apply it whenever possible.
It should be noted that these findings may not be generalized to less polar solvents and/or less charged solutes. Also, in our previous work on nonlinear optical properties, we found that neglecting the dynamic solvent response was not a good approximation.

5. Conclusions and Outlook

In this work we have investigated the CD spectrum of [Co(en)$_3$]$^{3+}$ in water, using the DRF model, which is a polarizable QM/MM model. The implementation of the DRF model for CD spectra calculations based on TDDFT has been reviewed. The combination of DRF with TDDFT allows for a computationally attractive solution when the explicit solvent structure is of interest. The extension to CD spectra enable chiroptical properties of molecules in solution to be calculated. Classical polarizable MD simulations have been used to obtain snapshots of the solvent structure around the [Co(en)$_3$]$^{3+}$ solute. The final CD spectrum is then obtained as an average over the snapshot configurations. We have shown that the final spectrum converge quickly with respect to the number of configurations and that the required number of snapshots was on the order of 50. Using mixed coarse/fine-grained parallel computation this kind of averaging can be obtained within a few hours of turnaround time in a routine fashion.

The DRF results were compared with results obtained from the much simpler COSMO model. Both models predict similar blue shifts of the CD bands above $35 \cdot 10^3$ cm$^{-1}$, although larger shifts are found with the COSMO model. None of the models is in perfect agreement with the experiments, since all the calculated intensities are much larger than what is found experimentally. Also, both theoretical methods predict a weak band at $\sim 40 \cdot 10^3$ cm$^{-1}$, which is not visible experimentally. A very strong sensitivity to the local structure of the solvent can be ruled out since the DRF results did not show a significant lowering of this band. Using DRF, it was shown that almost all the solvent effects arise from ground-state solvation. Thus, ignoring the dynamic solvent response is a good approximation for this system. The findings are likely to be transferable to other highly charged systems in polar solvents.

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