Introduction VROA MChD

# Vibronic effects on spectroscopic properties of metal complexes

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Introduction VROA MChD

# Outline



- 2 VROA
  - Theory
  - Computational Details
  - Results



- Theory
- Computational Details
- Results

# Outline for section 1

#### 1 Introduction

#### 2 VROA

- Theory
- Computational Details
- Results

#### 3 MChD

- Theory
- Computational Details
- Results

# Vibrational Raman optical activity (VROA)

- VROA is among the most recently developed chiroptical methods
- Measures the difference between left-/right-circularly polarized inelastically scattered light
- ROA studies have been found in protein structure analysis and transition metal complexes



# VROA cntd.

- Nafie<sup>1</sup> developed a two-state model where the resonance ROA intensities become mono-signate
- $\bullet\,$  Confirmed by Jensen, et al ^2 for  ${\rm H_2O_2}$  and (S)-methyloxirane
- Merten, et al<sup>3</sup> found that for bis-(trifluoroacetylcamphorato)copper(II) the RROA spectrum remains bi-signate



- <sup>1</sup> Nafie, et al Chem. Phys. **1996**, 205, 309–322
- <sup>2</sup> Jensen, et al J. Chem. Phys. **2007**, 127, 134101
- <sup>3</sup> Merten, et al J. Phys. Chem. **2012**, 116, 7329–7336

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# Induced OA

- It is possible to induce OA on molecules by applying an external magnetic field
- Common application is magnetic circular dichroism (MCD)
- MCD is similar to natural CD (NCD) where the differential absorption of left-/right-circularly polarized light is measured
- No information regarding the absolute configuration can be extracted



# Magneto-chiral dichroism (MChD)

- Unlike MCD, MChD was developed as an enantioselective technique
- Unlike MCD and NCD, the propagated light can be unpolarized
- Performing accurate measurements of MChD proves difficult as the MCD and NCD effects in the NIR region are much more dominant
- Will show that we get good agreement of the MChD spectra of  $[Ni(en)_3]^{2+}$  to experiment

# Outline for section 2

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#### Vibrational Raman optical activity

• The transition tensors can be expressed as geometric derivatives of the molecular properties

$$\Theta^{p}\Lambda^{p} = \langle 0|\Theta|1_{p}\rangle \langle 1_{p}|\Lambda|0\rangle = \frac{\partial\Theta}{\partial Q_{p}} \bigg|_{0} \left| \frac{\partial\Lambda}{\partial Q_{p}} \right|_{0}$$

- $\Theta$  and  $\Lambda$  can be:
  - $\alpha_{\alpha\alpha}$ : dipole-dipole polarizability transition tensor
  - $G'_{\alpha\beta}$ : electric dipole-magnetic dipole polarizability transition tensor
  - $A_{\gamma\delta\beta}$ : electric dipole-electric quadrupole polarizability transition tensor

# VROA cntd.

• The ROA intensities for a backscattering setup are calculated by

$$I^{R}(180^{\circ}) - I^{L}(180^{\circ}) = \Delta \frac{d\sigma}{d\Omega}(180^{\circ}) = K_{p} \left[ \frac{48(\beta(G')_{p}^{2} + \beta(A)_{p}^{2}/3)}{90c} \right]$$

Where

$$\beta(G')_p^2 = \operatorname{Im}\left(i\frac{3\alpha_{\alpha\beta}^p G'_{\alpha\beta}^{p*} - \alpha_{\alpha\alpha}^p G'_{\beta\beta}^{p*}}{2}\right)$$
$$\beta(A)_p^2 = \operatorname{Re}\left(\frac{1}{2}\omega\alpha_{\alpha\beta}^p \epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}^{p*}\right)$$

$$K_{p} = \frac{\pi^{2}}{\epsilon_{0}^{2}} (\tilde{\nu}_{\rm in} - \tilde{\nu}_{p})^{4} \frac{h}{8\pi^{2}c\tilde{\nu}_{p}} \frac{1}{1 - \exp[-hc\tilde{\nu}_{p}/k_{B}T]}$$

# **ROA** calculations

- Optimizations of  $[Co(en)_3]^{3+}$  and  $[Rh(en)_3]^{3+}$  were performed with the Gaussian program package
- A B3LYP hybrid functional along with a def2-TZVP Gaussian-type basis set was used. A 28-electron ECP was used for Rh.
- Linear response tensors were calculated with the KS response module of NWChem
- Calculation of the ROA intensities was performed with the *Exatomic* program package developed by current and former group members

Introduction **Computational Details** VROA MChD Results

Vibronic effects

# $\overline{\text{ROA}}$ calculations for $[\text{Rh(en)}_3]^{3+}$

- Calculated at 532 nm (2.331 eV) wavelength
- *lel*<sub>3</sub> structure agrees well with experimental spectrum
- Agrees with findings by Humbert-Droz, et  $al^4$



#### **ROA** calculations

- The incident wavelength energy falls far below the lowest electronic excitation energy of  $[Rh(en)_3]^{3+}$  at 320 nm (3.871 eV)
- For  $[Co(en)_3]^{3+}$  the lowest calculated electronic transitions happen at 476 nm (2.605 eV) and 481 nm (2.578 eV)
- The incident laser wavelength falls within the near-resonance domain

- Performed a scan of different incident wavelengths from 425 nm to 1319 nm for  $[Co(en)_3]^{3+}$
- All spectra normalized to the strongest peak in the 1319 nm spectrum
- ROA intensities rise sharply as the incident wavelength comes closer to the electronic excitation wavelength<sup>5</sup>



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<sup>5</sup> Abella; Ludowieg; and Autschbach, *Chirality* **2020**, *32*, 741–752

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#### Outline for section 3

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#### Vibronic coupling

• Calculate vibronic properties,  $\Lambda$ , with the Herzberg-Teller approximation

$$\mathbf{\Lambda}_{1,2} = \sum_{p}^{M} \left\langle \phi_{1} | Q_{p} | \phi_{2} \right\rangle \frac{\partial \mathbf{\Lambda}_{1,2}^{e}\left(Q\right)}{\partial Q_{p}} \bigg|_{0}$$

• Derivative determined by a Sum-over states perturbation theory approach

$$\begin{split} \frac{\partial \mathbf{\Lambda}_{1,2}^{e}\left(Q\right)}{\partial Q_{p}} &= \sum_{k \neq 1} \left\langle \psi_{k}^{0} | \mathbf{\Lambda}_{1,2}^{e} | \psi_{2}^{0} \right\rangle \frac{\left\langle \psi_{1}^{0} | \partial H / \partial Q_{p} | \psi_{k}^{0} \right\rangle}{E_{1}^{0} - E_{k}^{0}} \\ &+ \sum_{k \neq 2} \left\langle \psi_{1}^{0} | \mathbf{\Lambda}_{1,2}^{e} | \psi_{k}^{0} \right\rangle \frac{\left\langle \psi_{k}^{0} | \partial H / \partial Q_{p} | \psi_{2}^{0} \right\rangle}{E_{2}^{0} - E_{k}^{0}} \end{split}$$

## Vibronic coupling

- The terms  $\langle \psi_i^0 | \partial H / \partial Q_p | \psi_j^0 \rangle$ , in practice, are calculated by finite difference as  $\partial \langle \psi_i^0 | H | \psi_j^0 \rangle / \partial Q_p$  using a 'floating' atomic orbital basis<sup>6</sup>.
- Spin-orbit coupling is introduced via

$$\mathbf{\Lambda}_{1,2}^{\mathrm{SO}} = \sum_{k,m} U_{1,k}^{0\dagger} \langle \phi_k | \mathbf{\Lambda}_{k,m}^{\mathrm{SF}} \left( Q \right) | \phi_m \rangle U_{m,2}^{0}$$

<sup>6</sup> Orlandi, J. Chem. Phys. **1976**, 44 277–280



#### Magneto Chiral Dichroism intensities

• MChD intensities can be calculated with the equations from Barron and Vrbancich<sup>7</sup>

$$g_{j}(\omega) = \frac{\omega\Gamma}{(\omega_{j}^{2} - \omega^{2})^{2} + \omega^{2}\Gamma^{2}}$$
$$n^{\prime\uparrow\uparrow} - n^{\prime\uparrow\downarrow} = \frac{2\mu_{0}c\rho_{N}B}{3\hbar} \left[\omega_{j}g_{j}(\omega)\frac{C_{1}}{k_{B}T} - \omega g_{j}(\omega)\frac{C_{2}}{k_{B}T}\right]$$
$$C_{1} = \frac{1}{d}\sum_{\alpha,\beta,\gamma}\epsilon_{\alpha,\beta,\gamma}\sum_{n}m_{n,n}^{\alpha}\operatorname{Re}\left[\mu_{n,j}^{\beta}m_{j,n}^{\gamma}\right]$$
$$C_{2} = \frac{\omega}{15d}\sum_{\alpha,\beta}\sum_{n}m_{n,n}^{\alpha}\operatorname{Im}\left[3\mu_{n,j}^{\beta}\Theta_{j,n}^{\beta,\alpha} - \mu_{n,j}^{\alpha}\Theta_{j,n}^{\beta,\beta}\right]$$

<sup>7</sup> Barron and Vrbancich, *Molecular Physics* **1984**, *51*, 715–730

# Kohn-Sham Density Functional Theory

- KS-DFT calculations performed with the Gaussian program package
- Optimization and analytical frequency calculations performed with the hybrid B3LYP functional
- A Stuttgart-Dresden-Bonn relativistic ECP and a matching Gaussian-type valence basis set was used for Ni, and the 6-311+G(d) basis for all other atoms
- Wave-function theory calculations were performed on geometries from X-ray crystal structures, followed by optimization of the hydrogen positions with KS-DFT

#### Wave-Function Theory

- Calculations performed within the restricted active space (RAS) framework with a developers version of Molcas/OpenMolcas
- Scalar Relativistic effects were introduced via the second-order Douglass-Kroll-Hess Hamiltonian
- SR spin-free (SF) wavefunctions were determined in state-averaged RASSCF calculations
- Dynamic electron correlation was considered by performing second-order perturbation theory (PT2) calculations
- Spin-orbit coupling introduced via RAS state interaction (RASSI) among the spin-free states
- Diagonal elements of the SF part of the Hamiltonian were 'dressed' with PT2 energies





• Calculated (right) agrees well with experimental (left) spectrum in the peak intensity ratios for the peak c.a.  $19500 \text{ cm}^{-1}$ 

 $[Ni(en)_3]^{2+}$  vibrationally resolved ortho-axial absorption and CD spectrum



• Peak intensity ratios between calculated (right) agrees well with experimental (left) spectrum

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• Calculated (right) agrees very well with the experimental (left) spectrum  $^8$ 

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• Dashed line shows the purely electronic contributions to the MChD intensities

Atzori; Ludowieg; et al, *Sci. Adv.* **2021**, *7* Herbert D. Ludowieg Vibronic effects 23/24

# Thank you!

- Normal modes, frequencies and equilibrium structures for the ground and excited stated were assumed to be the same
- SO coupling Hamiltonian was calculated with a one-center approximation
- Electron spin contributions vanish as the matrix elements do not depend on vibrational distortions due to the one-center approximation

- Optimized with a CAS(12,12) made up of 5 3d orbitals, 5 pseudo-4d orbitals, and 2 ligand based orbitals corresponding to the  $e_g$  bonding pair in the  $O_h$  parentage symmetry
- Wavefunction parameters were generated for a RAS[20,2,2,6,5,5] made up of 6 ligand based orbitals in RAS1, 5 3d orbitals in RAS2, and 5 pseudo-4d in RAS3 generating a total of 40 triplet and 45 singlet states for the d-d and LMCT transitions