Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for *Where does the Raman optical activity of $[Rh(en)_3]^{3+}$ come from? Insight from a combined experimental and theoretical approach*

Marie Humbert-Droz, Patric Oulevey, Latévi Max Lawson Daku, Sandra Luber, Hans Hagemann and Thomas Bürgi

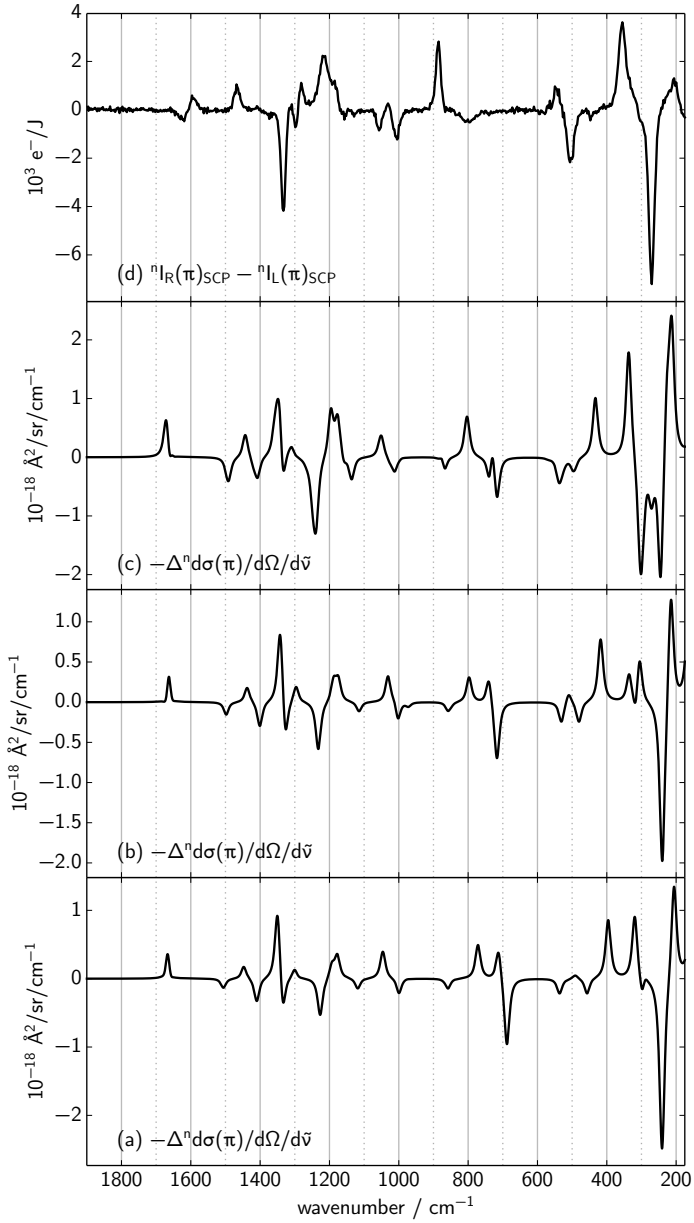

Figure 1 Variation of the density functional for the $\Lambda(\lambda\lambda\lambda)$ conformer. Basis set for all calculations: TZVP for atoms C, N, and H, CEP-121G for the Rh atom. Functionals: B3LYP (a), B3LYP-D (b), B3LYP-D and in combination with IEFPCM (c). For comparison: experiment (d). Backscattering, laser wavelength: 532 nm

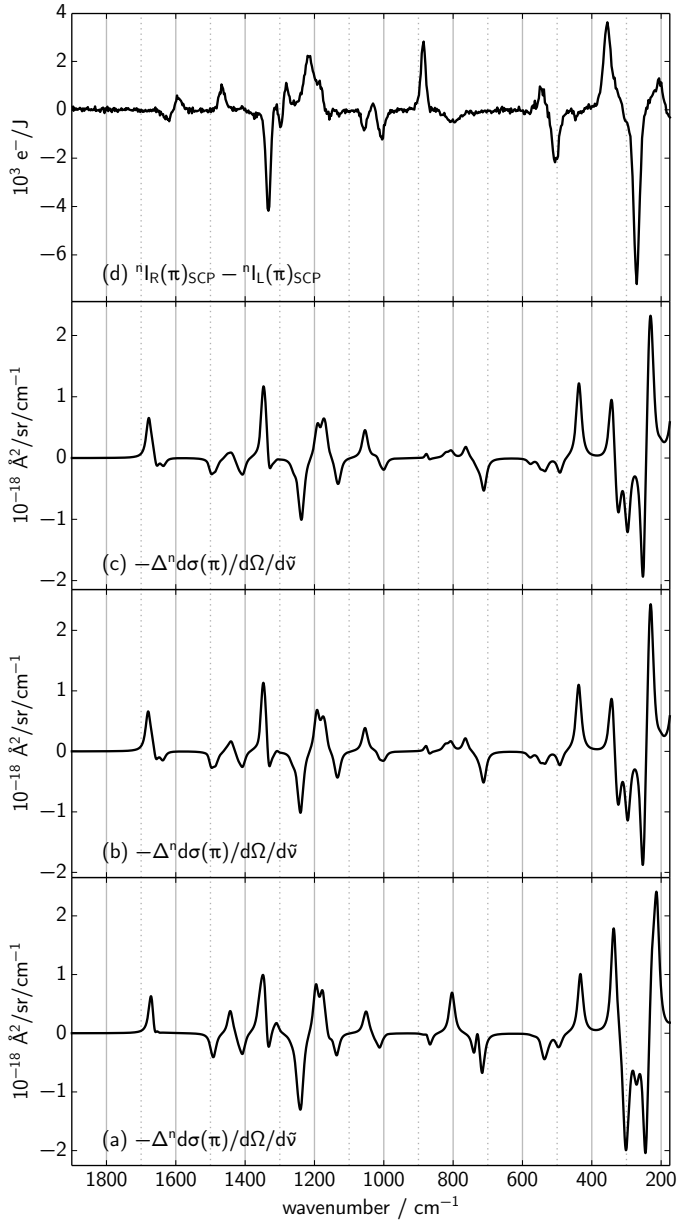

Figure 2 Variation of the basis setfor the $\Lambda(\lambda\lambda\lambda)$ conformer. For all calculations: B3LYP-D, IEFPCM. Basis sets: TZVP(C,N,H) and CEP-121G (Rh) (a), def2-TZVP (b), and def2-TZVPD (c). For comparison: experiment (d). Backscattering, laser wavelength: 532 nm

Atoms	Distance (Å)			Atoms	Angle (°)		
	Experiment	Calculation			Experiment	Calculation	
		gas	PCM			gas	PCM
Rh-N1	2.067	2.146	2.115	N1-Rh-N2	83.6	80.8	81.9
Rh-N2	2.056	2.146	2.116	Rh-N1-C1	107.3	109.9	109.0
N1-C1	1.481	1.510	1.499	Rh-N2-C2	108.9	109.9	109.3
N2-C2	1.502	1.510	1.500	N1-C1-C2	107.7	108.7	108.6
C1-C2	1.52	1.512	1.512	N2-C2-C1	106.8	108.7	108.4
N1-H(N1)1	0.89	1.020	1.018	Rh-N1-H(N1)1	108	115.0	114.1
N1-H(N1)2	0.87	1.021	1.019	Rh-N1-H(N1)2	104	110.2	110.0
				C1-N1-H(N1)1	106	108.6	109.0
				C1-N1-H(N1)2	108	108.6	109.5
				H(N1)1-N1-H(N1)2	122	104	105.1
N2-H(N2)1	0.89	1.021	1.019	Rh-N2-H(N2)1	106	110.2	109.7
N2-H(N2)2	0.87	1.020	1.017	Rh-N2-H(N2)2	112	115.0	114.2
				C2-N2-H(N2)1	111	108.6	109.3
				C2-N2-H(N2)2	109	108.6	108.9
				H(N2)1-N2-H(N2)2	110	104.3	105.2
C1-H(C1)1	1.02	1.091	1.089	N1-C1-H(C1)1	107	108.1	107.8
C1-H(C1)2	1.07	1.092	1.089	N1-C1-H(C1)2	110	110.3	110.2
				C2-C1-H(C1)1	114	111.4	110.5
				C2-C1-H(C1)2	111	111.1	111.1
				H(C1)1-C1-H(C1)2	108	107.2	108.5
C2-H(C2)1	1.06	1.092	1.089	N2-C2-H(C2)1	107	110.3	110.1
C2-H(C2)2	1.01	1.091	1.089	N2-C2-H(C2)2	107	108.1	107.9
				C1-C2-H(C2)1	108	111.1	110.9
				C1-C2-H(C2)2	108	111.4	111.0
				H(C2)1-C2-H(C2)2	120	107.2	108.3

Table 1 Comparison of experimental [1] and calculated geometry parameters for the $\Lambda(\lambda\lambda\lambda)$-$[Rh(en)_3]^{3+}$ conformer. Values listed for the gas phase are obtained at the B3LYP/def2-TZVP, and for PCM at the B3LYP-D2/def2-TZVP level of theory

Atoms	Distance (Å)					Atoms	Angle (°)				
	Experiment	Calculation					Experiment	Calculation			
		ligand δ		ligand λ				ligand δ		ligand λ	
		gas	PCM	gas	PCM			gas	PCM	gas	PCM
Rh-N1	2.067	2.134	2.106	2.134	2.106	N1-Rh-N2	83.6	81.1	82.2	81.0	82.2
Rh-N2	2.056	2.134	2.106	2.136	2.104	Rh-N1-C1	107.3	109.8	109.0	109.9	108.7
N1-C1	1.481	1.508	1.497	1.507	1.496	Rh-N2-C2	108.9	109.8	109.0	109.9	109.2
N2-C2	1.502	1.508	1.497	1.508	1.497	N1-C1-C2	107.7	108.6	108.5	108.6	108.4
C1-C2	1.52	1.510	1.511	1.511	1.511	N2-C2-C1	106.8	108.6	108.5	108.6	108.4
N1-H(N1)1	0.89	1.020	1.018	1.020	1.017	Rh-N1-H(N1)1	108	111.6	111.8	115.1	114.3
N1-H(N1)2	0.87	1.020	1.018	1.021	1.019	Rh-N1-H(N1)2	104	113.8	112.8	110.0	110.5
						C1-N1-H(N1)1	106	108.4	109.1	108.8	109.0
						C1-N1-H(N1)2	108	108.5	108.8	108.5	109.1
						H(N1)1-N1-H(N1)2	122	104.4	105.2	104.1	105.0
N2-H(N2)1	0.89	1.020	1.018	1.021	1.019	Rh-N2-H(N2)1	106	113.8	112.8	110.2	109.4
N2-H(N2)2	0.87	1.020	1.018	1.020	1.018	Rh-N2-H(N2)2	112	111.7	111.8	115.2	114.4
						C2-N2-H(N2)1	111	108.5	108.8	108.4	109.3
						C2-N2-H(N2)2	109	108.4	109.1	108.5	109.2
						H(N2)1-N2-H(N2)2	110	104.4	105.2	104.3	105.0
C1-H(C1)1	1.02	1.091	1.089	1.091	1.089	N1-C1-H(C1)1	107	110.3	110.2	108.1	107.9
C1-H(C1)2	1.07	1.091	1.088	1.091	1.089	N1-C1-H(C1)2	110	108.0	107.6	110.3	110.2
						C2-C1-H(C1)1	114	111.2	111.1	111.3	110.9
						C2-C1-H(C1)2	111	111.5	110.9	111.2	111.0
						H(C1)1-C1-H(C1)2	108	107.2	108.4	107.2	108.4
C2-H(C2)1	1.06	1.091	1.088	1.091	1.089	N2-C2-H(C2)1	107	108.0	107.6	110.3	110.2
C2-H(C2)2	1.01	1.091	1.089	1.091	1.089	N2-C2-H(C2)2	107	110.3	110.2	108.1	107.9
						C1-C2-H(C2)1	108	111.5	110.9	111.2	111.1
						C1-C2-H(C2)2	108	111.2	111.1	111.4	110.5
						H(C2)1-C2-H(C2)2	120	107.2	108.4	107.2	108.6

Table 2 Comparison of experimental [1] and calculated geometry parameters for the $\Lambda(\lambda\lambda\delta)$-$[Rh(en)_3]^{3+}$ conformer. Values listed for the gas phase are obtained at the B3LYP/def2-TZVP, and for PCM at the B3LYP-D2/def2-TZVP level of theory

Atoms	Distance (Å)					Atoms	Angle (°)				
	Experiment	Calculation					Experiment	Calculation			
		ligand δ		ligand λ				ligand δ		ligand λ	
		gas	PCM	gas	PCM			gas	PCM	gas	PCM
Rh-N1	2.067	2.134	2.102	2.135	2.107	N1-Rh-N2	83.6	81.2	82.4	81.1	82.0
Rh-N2	2.056	2.134	2.104	2.135	2.108	Rh-N1-C1	107.3	109.8	108.6	109.8	108.7
N1-C1	1.481	1.509	1.497	1.508	1.496	Rh-N2-C2	108.9	109.5	109.0	109.8	108.7
N2-C2	1.502	1.508	1.498	1.508	1.496	N1-C1-C2	107.7	108.6	108.2	108.6	107.9
C1-C2	1.52	1.510	1.511	1.511	1.511	N2-C2-C1	106.8	108.6	108.6	108.6	107.9
N1-H(N1)1	0.89	1.020	1.018	1.020	1.018	Rh-N1-H(N1)1	108	112.1	112.1	115.3	114.2
N1-H(N1)2	0.87	1.020	1.018	1.020	1.019	Rh-N1-H(N1)2	104	113.5	112.7	110.1	110.4
						C1-N1-H(N1)1	106	108.5	109.0	108.8	109.6
						C1-N1-H(N1)2	108	108.6	109.3	108.4	108.7
						H(N1)1-N1-H(N1)2	122	104.2	105.1	104.2	105.1
N2-H(N2)1	0.89	1.020	1.018	1.021	1.019	Rh-N2-H(N2)1	106	114.1	113.0	110.1	110.4
N2-H(N2)2	0.87	1.020	1.018	1.020	1.018	Rh-N2-H(N2)2	112	111.7	111.6	115.3	114.2
						C2-N2-H(N2)1	111	108.4	108.8	108.4	108.7
						C2-N2-H(N2)2	109	108.5	109.2	108.8	109.6
						H(N2)1-N2-H(N2)2	110	104.4	105.2	104.2	105.1
C1-H(C1)1	1.02	1.091	1.089	1.091	1.089	N1-C1-H(C1)1	107	110.3	110.2	108.2	108.2
C1-H(C1)2	1.07	1.091	1.089	1.091	1.089	N1-C1-H(C1)2	110	108.0	107.7	110.3	110.3
						C2-C1-H(C1)1	114	111.2	111.1	111.3	110.5
						C2-C1-H(C1)2	111	111.5	111.2	111.2	111.3
						H(C1)1-C1-H(C1)2	108	107.2	108.4	107.3	108.6
C2-H(C2)1	1.06	1.091	1.088	1.091	1.089	N2-C2-H(C2)1	107	107.9	107.4	110.3	110.3
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						C1-C2-H(C2)1	108	111.5	110.7	111.2	111.3
						C1-C2-H(C2)2	108	111.2	111.2	111.3	110.5
						H(C2)1-C2-H(C2)2	120	107.3	108.6	107.3	108.6

Table 3 Comparison of experimental [1] and calculated geometry parameters for the $\Lambda(\lambda\delta\delta)$-$[Rh(en)_3]^{3+}$ conformer. Values listed for the gas phase are obtained at the B3LYP/def2-TZVP, and for PCM at the B3LYP-D2/def2-TZVP level of theory

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				C1-N1-H(N1)1	106	108.5	108.8
				C1-N1-H(N1)2	108	108.5	109.2
				H(N1)1-N1-H(N1)2	122	104.2	104.8
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N2-H(N2)2	0.87	1.020	1.018	Rh-N2-H(N2)2	112	112.2	112.1
				C2-N2-H(N2)1	111	108.5	109.0
				C2-N2-H(N2)2	109	108.5	109.1
				H(N2)1-N2-H(N2)2	110	104.2	104.9
C1-H(C1)1	1.02	1.091	1.089	N1-C1-H(C1)1	107	110.3	110.3
C1-H(C1)2	1.07	1.091	1.089	N1-C1-H(C1)2	110	107.9	107.6
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				H(C1)1-C1-H(C1)2	108	107.3	108.6
C2-H(C2)1	1.06	1.091	1.089	N2-C2-H(C2)1	107	107.9	107.5
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				C1-C2-H(C2)1	108	111.5	110.9
				C1-C2-H(C2)2	108	111.2	111.1
				H(C2)1-C2-H(C2)2	120	107.3	108.6

Table 4 Comparison of experimental [1] and calculated geometry parameters for the $\Lambda(\delta\delta\delta)$-$[Rh(en)_3]^{3+}$ conformer. Values listed for the gas phase are obtained at the B3LYP/def2-TZVP, and for PCM at the B3LYP-D2/def2-TZVP level of theory

Table 5 Comparison of positions (cm^{-1}) and signs (+/–) of Raman optical activity bands for the four calculated conformers of the Λ-Rhodium-*tris*-ethylenediamine complex with experimental values

arb. nb.	$\Lambda(\lambda\lambda\lambda)$		$\Lambda(\lambda\lambda\delta)$		$\Lambda(\lambda\delta\delta)$		$\Lambda(\delta\delta\delta)$		Experiment	
1	146	+	169	–	188	+	214	+	203	+
2	245	–	261	–	255	–	274	–	269	–
3	304	–	303	–	346	+	345	+	355	+
	335	+	326	+	347	–	360	+	355	+
	338	+	336	+	365	+	367	+	355	+
4	491	–	489	–	493	–	497	–	502	–
	498	–	500	–	497	–	499	–	502	–
5	524	–	526	+	534	+	541	+	546	+
6	873	+	874	–	876	–	876	+	884	+
	874	–	881	+	880	–	885	+	884	+
	875	–	881	–	883	+	887	+	884	+
	882	–	887	–	889	+	887	+	884	+
7	1013	–	1021	–	1010	–	1013	–	1005	–
	1017	+	1029	+	1015	–	1021	–	1005	–
8	1050	+	1053	+	1047	+	1048	–	1057	–
	1050	+	1053	+	1053	–	1051	–	1057	–
	1055	+	1056	–	1054	–	1054	–	1057	–
9	1239	–	1222	–	1235	–	1235	–	1215	+
	1248	–	1233	+	1238	+	1245	+	1215	
10	1350	–	1343	+	1342	+	1346	–	1332	–
	1351	+	1350	+	1344	–	1346	–	1332	–
	1358	+	1355	+	1350	+	1361	–	1332	–
	1360	+	1358	–	1352	–	1362	–	1332	–
11	1489	+	1489	+	1425	+	1500	–	1466	+
	1490	–	1491	–	1443	–	1500	+	1466	+
	1494	–	1501	+	1450	–	1504	–	1466	+
	1497	+	1503	+	1485	–	1504	+	1466	+
	1498	–	1525	–	1485	+	1508	+	1466	+
	1500	+	1525	–	1495	–	1509	–	1466	
12	1650	–	1642	+	1648	–	1650	–	1598	+
	1657	+	1645	–	1663	–	1659	–	1598	+
	1660	–	1655	+	1666	–	1672	–	1598	+
	1666	–	1655	–	1674	+	1686	+	1598	+
13	1670	+	1660	–	1686	–	1692	–	1617	–
	1672	+	1666	+	1711	+	1706	+	1617	–

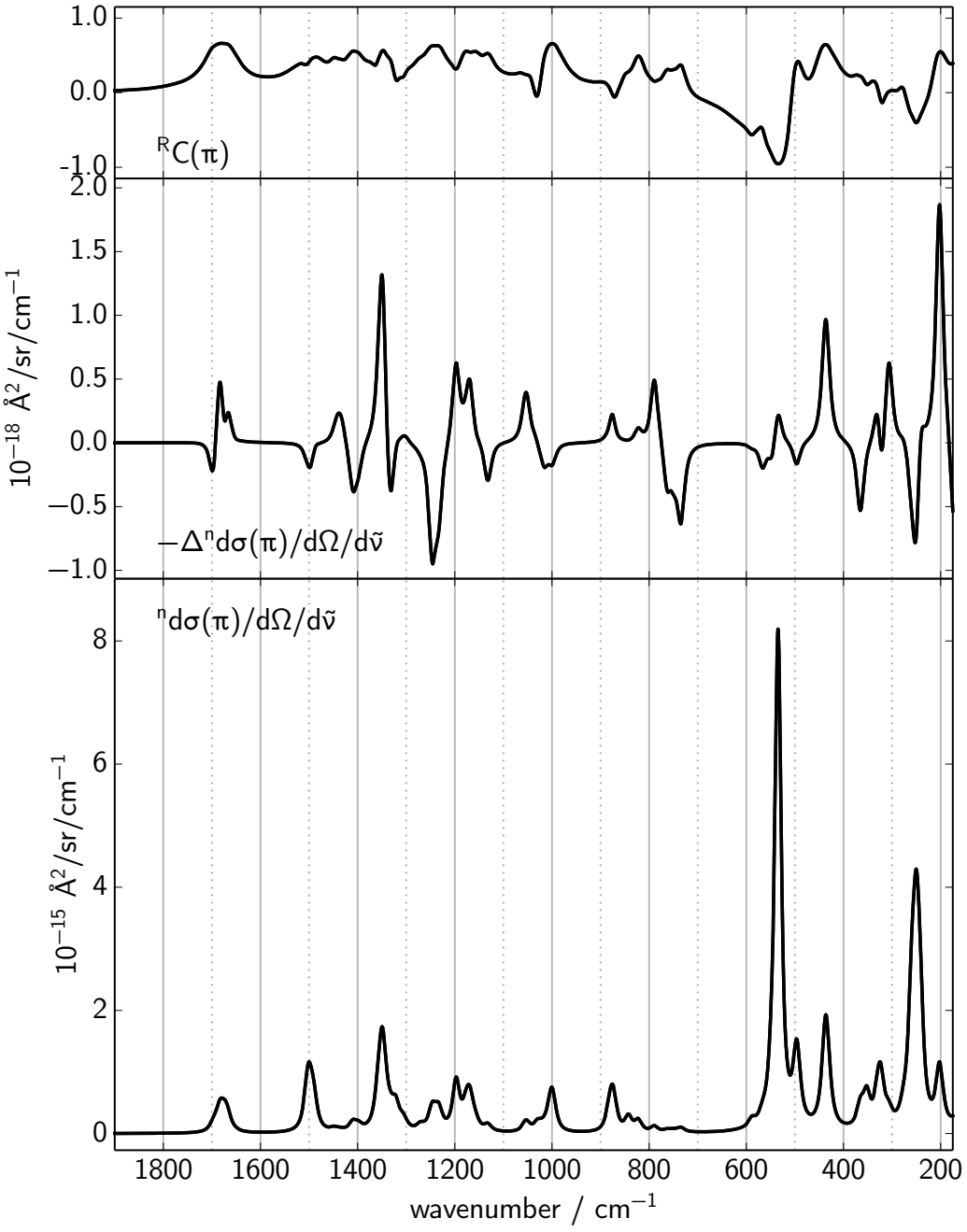


Figure 3 Raman, ROA, and degree of circularity spectra (*bottom* to *top*) of the calculated spectra of $\Lambda(\lambda\lambda\lambda)$ conformer. B3LYP-D/def2-TZVP/IEFPCM

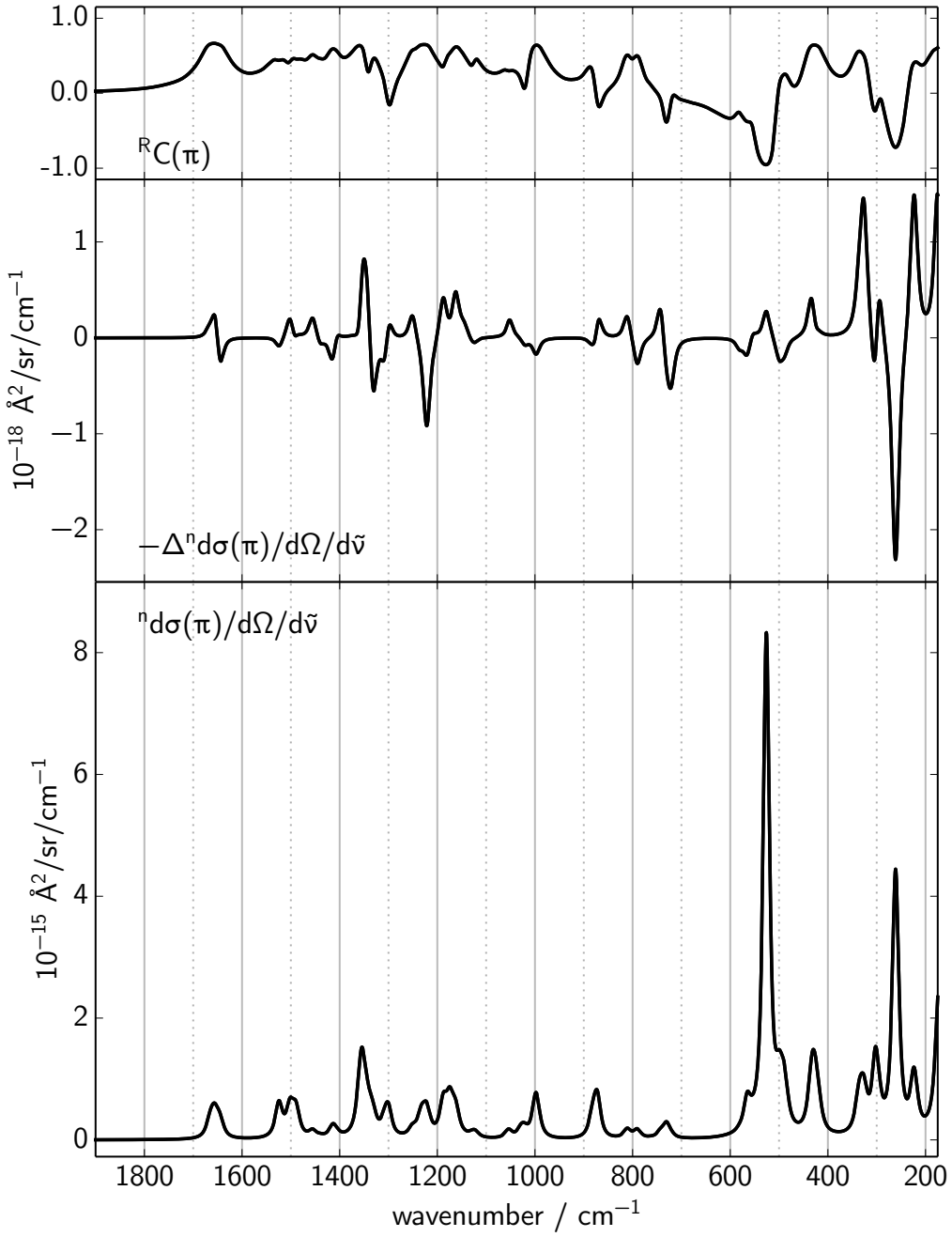


Figure 4 Raman, ROA, and degree of circularity spectra (*bottom* to *top*) of the calculated spectra of $\Lambda(\lambda\lambda\delta)$ conformer. B3LYP-D/def2-TZVP/IEFPCM

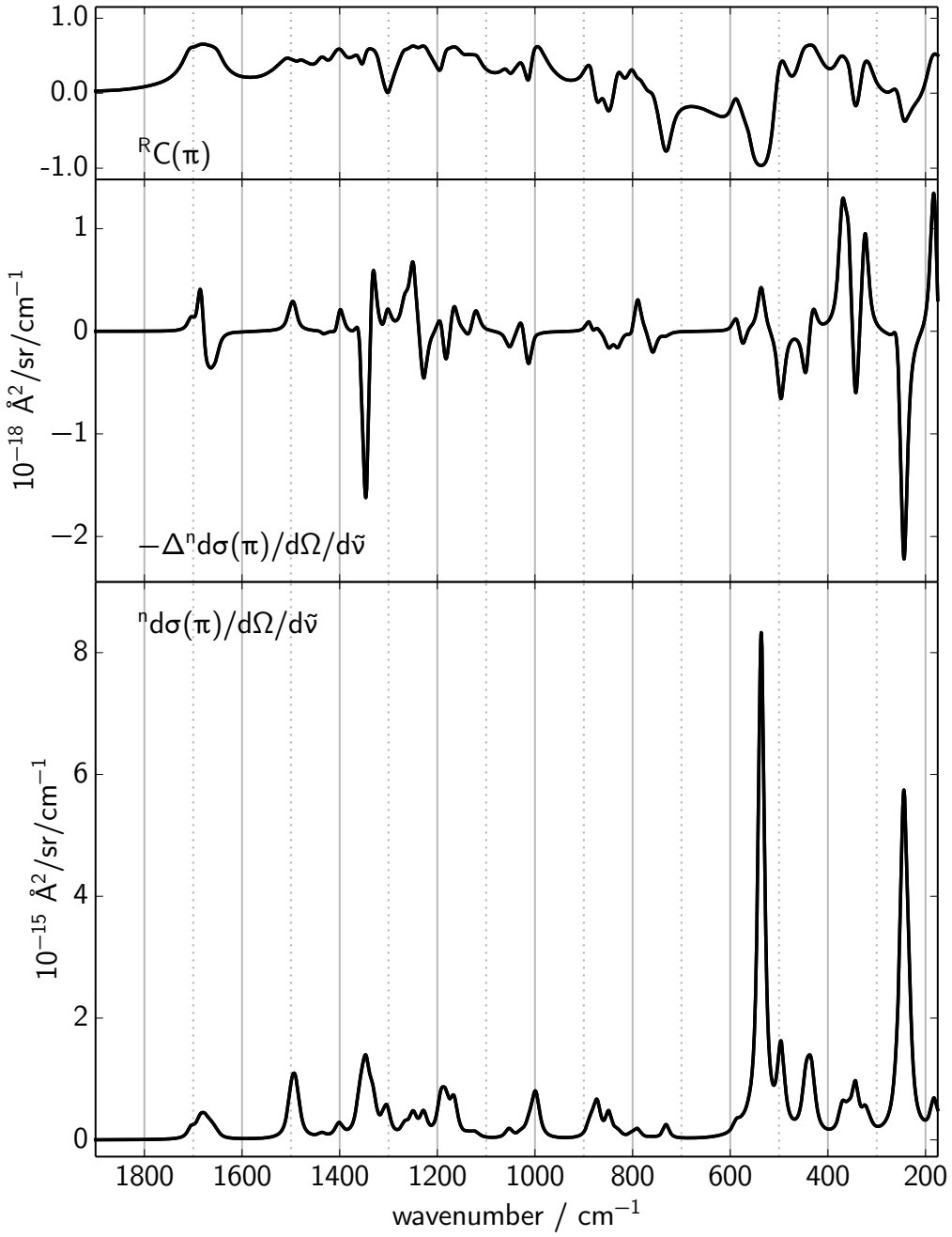


Figure 5 Raman, ROA, and degree of circularity spectra (*bottom* to *top*) of the calculated spectra of $\Lambda(\lambda\,\delta\,\delta)$ conformer. B3LYP-D/def2-TZVP/IEFPCM

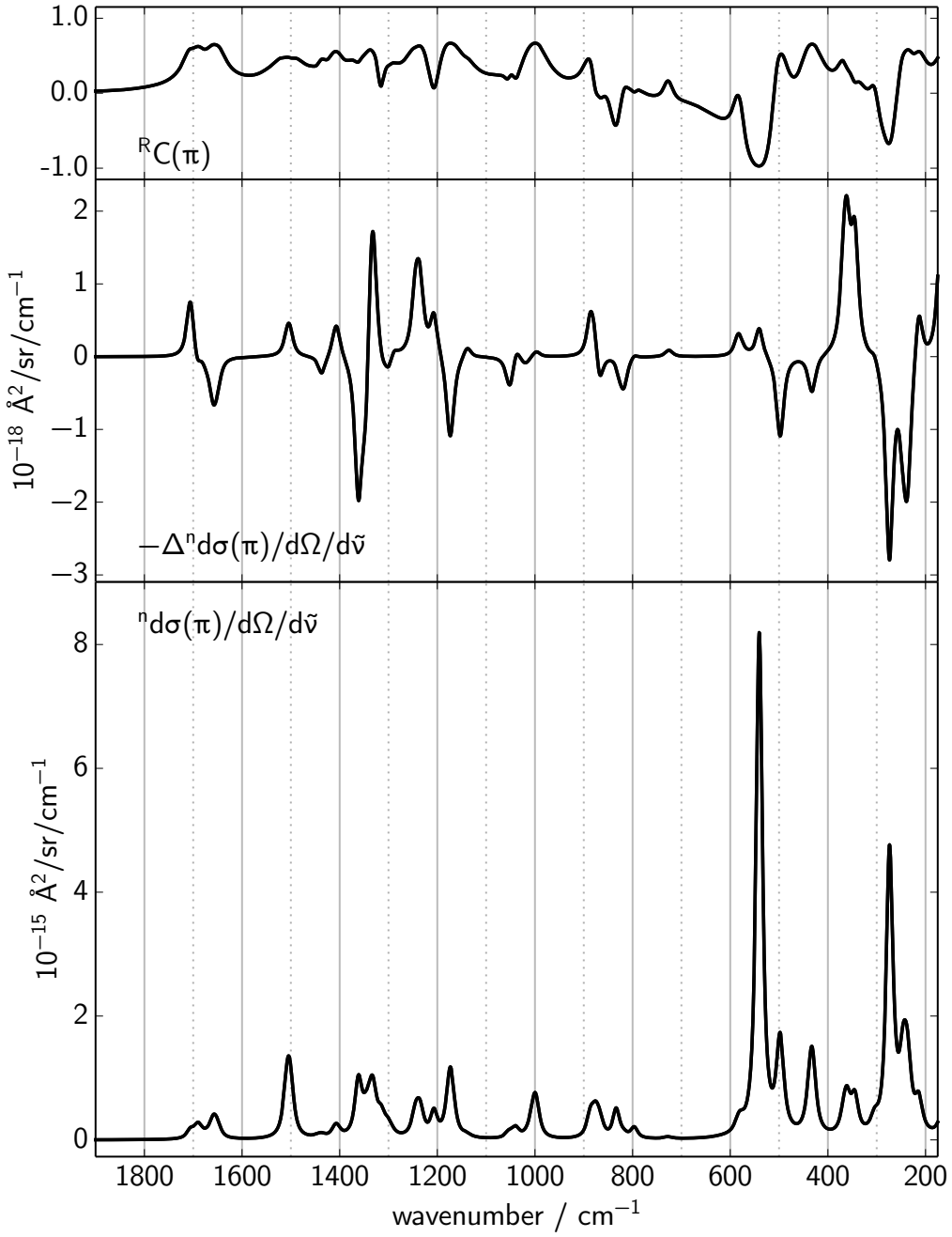
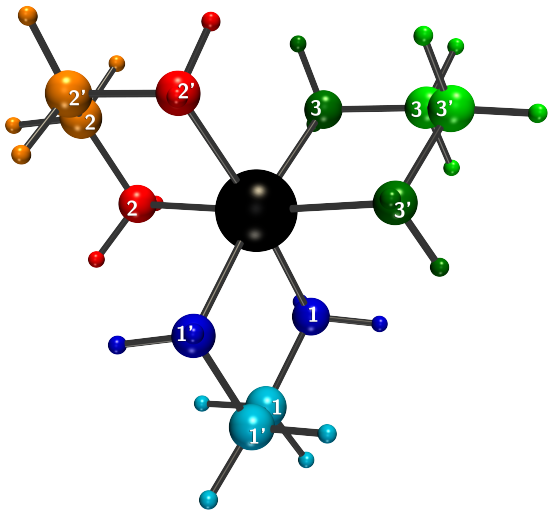
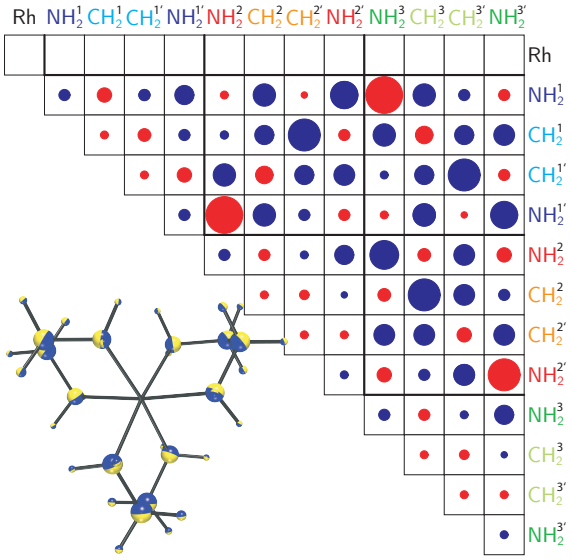


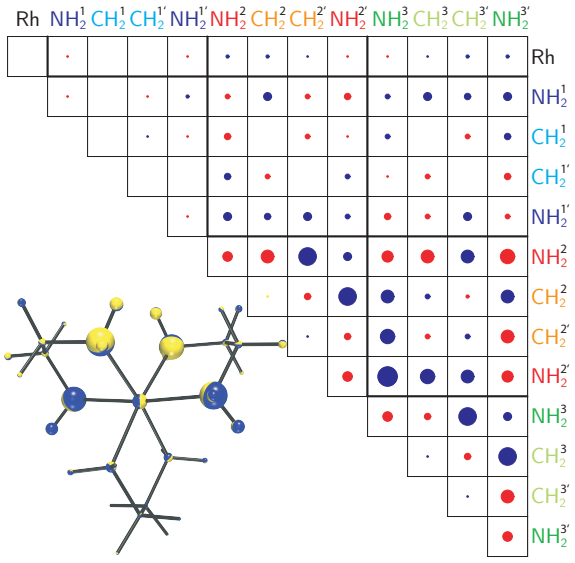
Figure 6 Raman, ROA, and degree of circularity spectra (*bottom* to *top*) of the calculated spectra of $\Lambda(\delta\delta\delta)$ conformer. B3LYP-D/def2-TZVP/IEFPCM



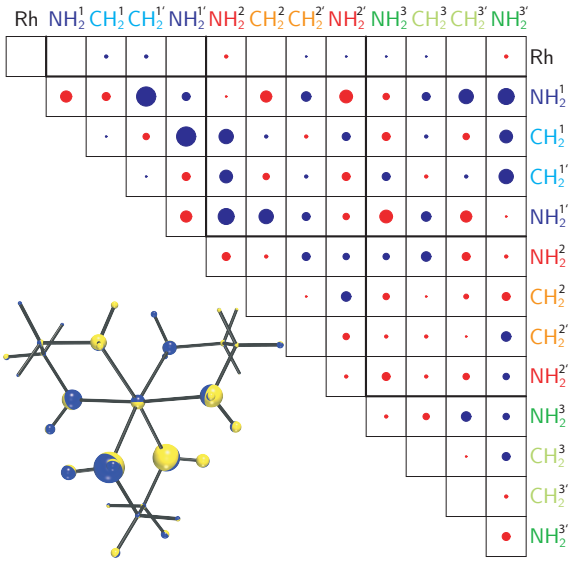
(a) atom grouping



(b) ROA, sf:1.0,
en breathing (ν_2)

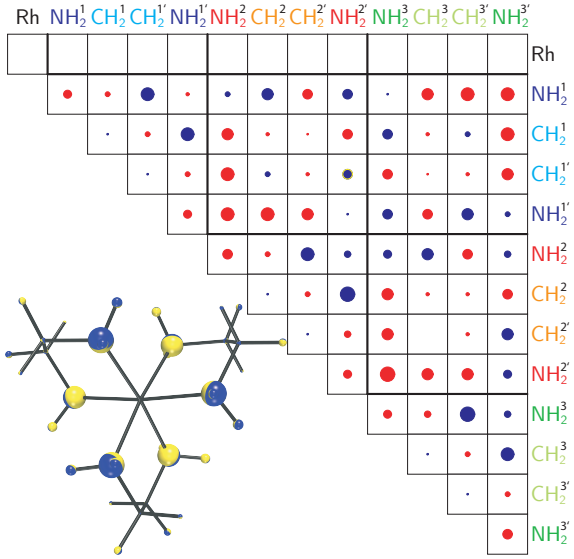


(c) ROA, sf:1.0,
out-of-phase en scissoring (ν_4^a)

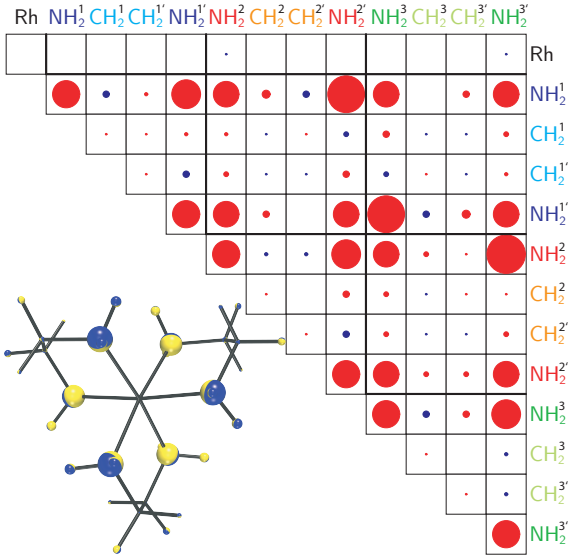


(d) ROA, sf:1.0,
out-of-phase en scissoring (ν_4^b)

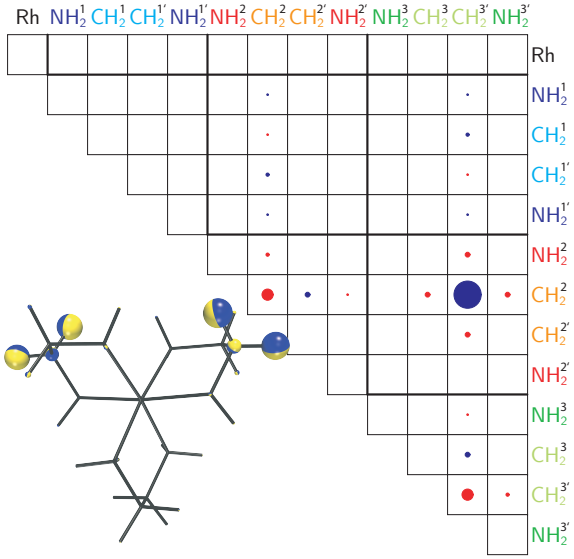
Figure 7 (a) shows the allocation of atoms into the defined groups, (b)–(j) show GCMs for a chosen invariant combination (ROA or Raman) and scaling factor (sf). A description of the vibration is also given, followed by the identifier of the normal mode in brackets. For each GCM the surface area of illustrated circles are proportional to the value of the matrix element and the color indicate their sign (blue: negative, red:positive)



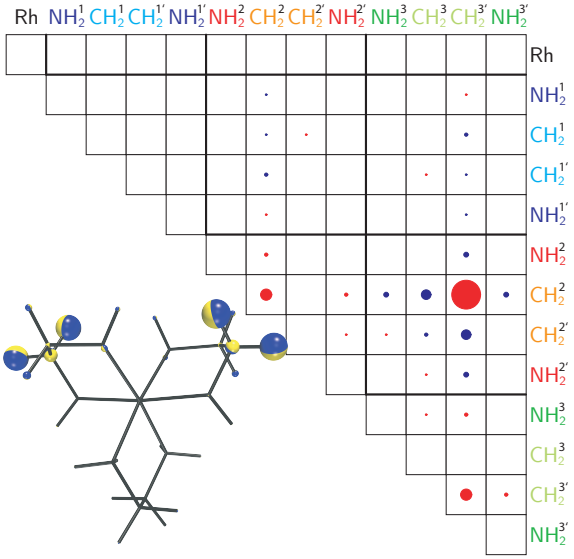
(e) ROA, sf:1.0,
in-phase en scissoring (ν_5)



(f) Raman,
in-phase en scissoring (ν_5)

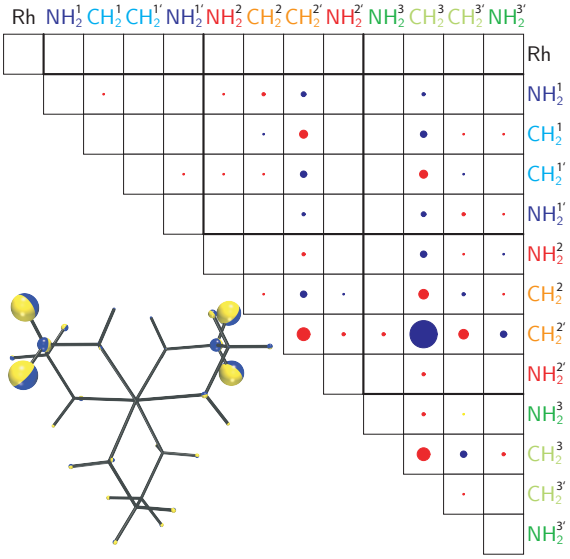


(g) ROA, sf:1.0,
in-phase $CH_2^{2-3'}$ scissoring (ν_{11}^a)

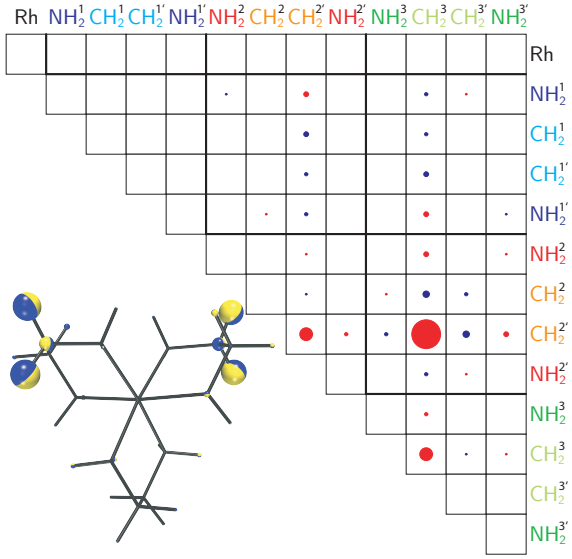


(h) ROA, sf:1.0,
out-of-phase $CH_2^{2-3'}$ scissoring (ν_{11}^b)

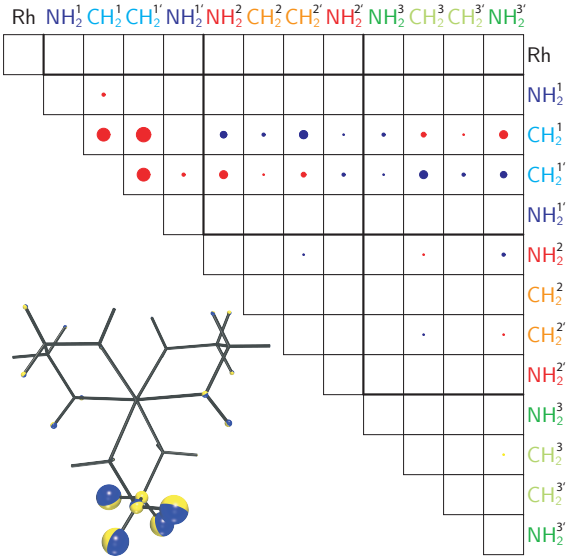
Figure 7 Continued



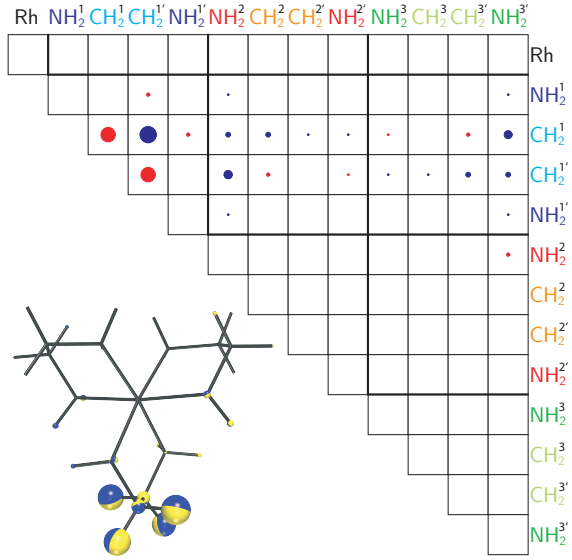
(i) ROA, sf:1.0,
out-of-phase $CH_2^{2'-3}$ scissoring (ν_{11}^{c})



(j) ROA, sf:1.0,
in-phase $CH_2^{2'-3}$ scissoring (ν_{11}^{d})



(k) ROA, sf:1.0,
out-of-phase $CH_2^{1-1'}$ scissoring (ν_{11}^{e})



(l) ROA, sf:1.0,
in-phase $CH_2^{1-1'}$ scissoring (ν_{11}^{f})

Figure 7 Continued

Synthesis

$(+)_D$- and $(-)_D$-*tris*(ethylenediamine)-rhodium(III) chloride hydrate, $[Rh(en)_3]Cl_3 \cdot 3\,H_2O$, have been prepared according to the procedure described by Galsbøl[2]. Summarily, a mixture of ethylendiamine in slightly molar excess and water is drop-wise added to rhodium(III) chlorate trihydrate under ice cooling. After the addition, the reaction mixture is carefully heated and is allowed to reflux until the complete disappearance of rhodium chloride. The addition of ethanol to the cooled reaction mixture gives a precipitate, which is then dissolved by boiling. Upon cooling to room temperature, white crystals fall out of the yellow solution, which can be, after further cooling with ice, separated by filtration and washed repeatedly with 60%, 80%, and 96% ethanol. The crystals are dried in air. The yield of the synthesis can be increased by using the filtrate and the washing fractions, as described in the original work[2].
Eventually, the previously collected crystals are purified – the crude products are dissolved in hot water and remains removed using a filter with very high retention. The filtrate is heated and absolute ethanol is added before the boiling is reached; heating can be stopped, as soon as the solution got clear. Then a few drops of ethylenediamine monohydrate are added, the solution is slowly cooled to room temperature and then actively cooled with ice. The obtained crystals are finally washed two times with 80% ethanol and one time with 96% ethanol before dried at air.

Following also the original work[2], the enantioseparation was performed by precipitating a $Li\{(-)_D\text{-}-[Rh(en)_3]\}\{(+)-tartrate\}_2 \cdot 3\,H_2O$ double salt, which could be purified and converted into the chloride form. The $(+)_D-[Rh(en)_3]Cl_3$ is obtained as precipitate of the mother liquor upon addition of HCl and ethanol. For details it is referred to the original work.

References

[1] J. L. Sudmeier and G. L. Blackmer, *Inorg. Chem.*, 1971, **10**, 2010.

[2] F. Galsbøl, *Inorganic Sytheses*, 1970, **12**, 269–280.

ps	Rh-N^1	Rh-$N^{1'}$	Rh-N^2	Rh-$N^{2'}$	Rh-N^3	Rh-$N^{3'}$
00.0	2.099 Å	2.103 Å	2.096 Å	2.095 Å	2.098 Å	2.104 Å
02.5	2.102 Å	2.092 Å	2.092 Å	2.099 Å	2.108 Å	2.104 Å
05.0	2.111 Å	2.108 Å	2.098 Å	2.090 Å	2.091 Å	2.103 Å
07.5	2.095 Å	2.103 Å	2.100 Å	2.108 Å	2.098 Å	2.098 Å
10.0	2.095 Å	2.099 Å	2.094 Å	2.094 Å	2.090 Å	2.096 Å
12.5	2.097 Å	2.098 Å	2.102 Å	2.103 Å	2.097 Å	2.097 Å
15.0	2.094 Å	2.096 Å	2.095 Å	2.110 Å	2.099 Å	2.095 Å
17.5	2.111 Å	2.105 Å	2.093 Å	2.096 Å	2.098 Å	2.110 Å
20.0	2.096 Å	2.094 Å	2.096 Å	2.099 Å	2.100 Å	2.095 Å
22.5	2.100 Å	2.100 Å	2.109 Å	2.094 Å	2.100 Å	2.097 Å
25.0	2.094 Å	2.095 Å	2.109 Å	2.102 Å	2.102 Å	2.091 Å
27.5	2.093 Å	2.098 Å	2.104 Å	2.107 Å	2.101 Å	2.095 Å
30.0	2.100 Å	2.104 Å	2.105 Å	2.100 Å	2.097 Å	2.100 Å
32.5	2.097 Å	2.104 Å	2.114 Å	2.100 Å	2.098 Å	2.092 Å
mean	2.099 Å	2.100 Å	2.100 Å	2.100 Å	2.098 Å	2.098 Å
	2.099 Å		2.100 Å		2.098 Å	
	2.099 Å					

ps	$\angle$ $N^1RhN^{1'}$	$\angle$ $N^2RhN^{2'}$	$\angle$ $N^3RhN^{3'}$	$\angle$ $N^1C^1C^{1'}N^{1'}$	$\angle$ $N^2C^2C^{2'}N^{2'}$	$\angle$ $N^3C^3C^{3'}N^{3'}$
00.0	83.075°	82.577°	82.231°	55.689°	54.412°	54.590°
02.5	82.576°	82.999°	82.297°	54.208°	53.903°	52.191°
05.0	82.283°	82.666°	82.986°	54.347°	54.207°	55.307°
07.5	83.017°	82.484°	82.573°	54.790°	55.327°	55.300°
10.0	83.412°	83.085°	83.134°	55.073°	53.467°	54.360°
12.5	82.617°	82.224°	82.666°	52.090°	54.783°	53.637°
15.0	82.733°	82.536°	83.042°	51.955°	55.212°	55.085°
17.5	82.273°	82.732°	82.294°	53.146°	54.156°	56.323°
20.0	83.258°	83.018°	82.741°	54.274°	54.238°	55.929°
22.5	82.913°	82.313°	82.649°	55.262°	53.005°	54.466°
25.0	83.143°	81.420°	82.489°	54.489°	47.409°	54.636°
27.5	82.953°	82.427°	82.835°	55.114°	55.297°	54.928°
30.0	82.636°	82.702°	82.860°	55.843°	54.569°	53.058°
32.5	82.464°	82.429°	83.213°	55.217°	55.863°	55.264°
mean	82.811°	82.544°	82.715°	54.393°	53.989°	54.648°
	82.690°			54.343°		

Table 6 Characteristic structural parameters of the optimized $\Lambda(\delta\delta\delta)-[Rh(en)_3]^{3+}$ complex for the 14 snapshots of the BOMD simulation (0 ps – 32.5 ps) with first solvation sphere; IEFPCM used, theoretical level: B3LYP-D2/def2-TZVP. *top:* Rh−N bond lengths. *bottom:* bite angle $\beta = \angle$N−Rh−N and dihedral angle $\gamma = \angle$N−C−C−N. Superscripts for N and C indicate the en bridge on which the atoms are located (number) and on which side of the en bridge they are (potential apostrophe)

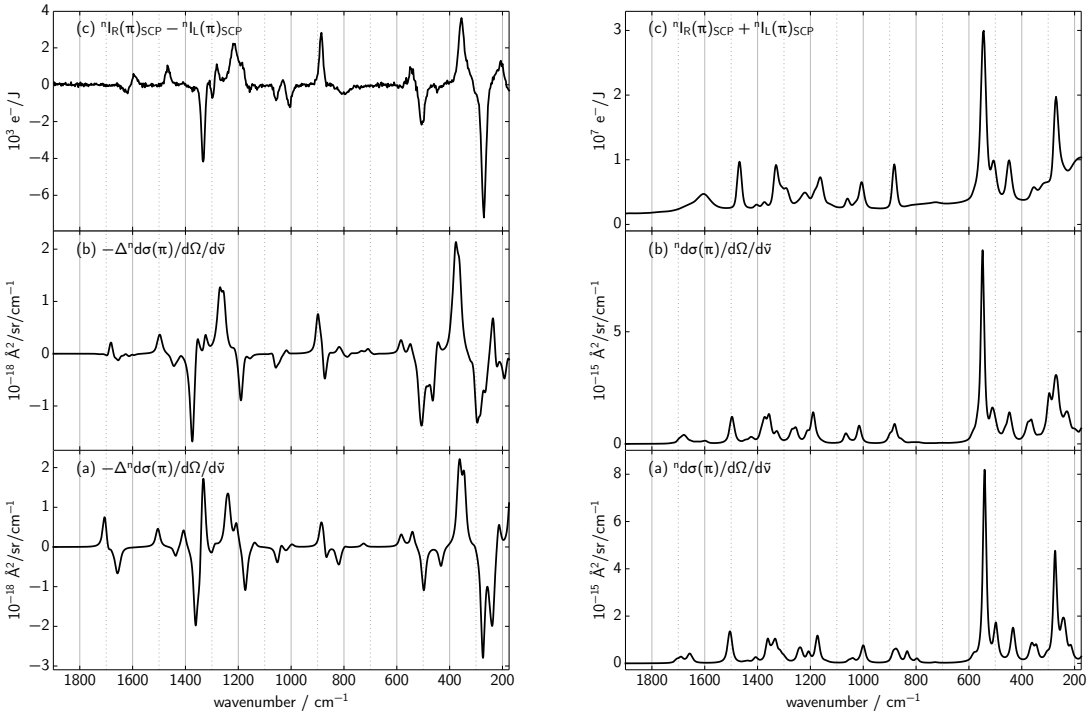


Figure 8 ROA (*left*) and Raman (*right*) spectra – comparison of $\Lambda(\delta\delta\delta)$−[Rh(en)$_3$]$^{3+}$ within the IEPCM model (a) and the mean theoretical spectra for the 14 AIMD snapshots of $\Lambda(\delta\delta\delta)$−[Rh(en)$_3$]$^{3+}$ with its first solvation sphere (within IEPCM) (b) with the experiment (c). One snapshot each 2.5 ps was taken till 32.5 ps ($[00.0, 32.5], \Delta = 2.5$); theoretical spectra weighted according to the Boltzmann distribution for the Free energies composed of the sum of electronic and thermal contributions: (0.0 ps: 0.70%, 2.5 ps: 4.78%, 5.0 ps: 78.29%, 7.5 ps: 1.02%, 10.0 ps: 0.03%, 12.5 ps: 0.01%, 15.0 ps: 0.19%, 17.5 ps: 0.62%, 20.0 ps: 2.37%, 22.5 ps: 0.54%, 25.0 ps: 0.09%, 27.5 ps: 1.04%, 30.0 ps: 0.49%, 32.5 ps: 9.82%)

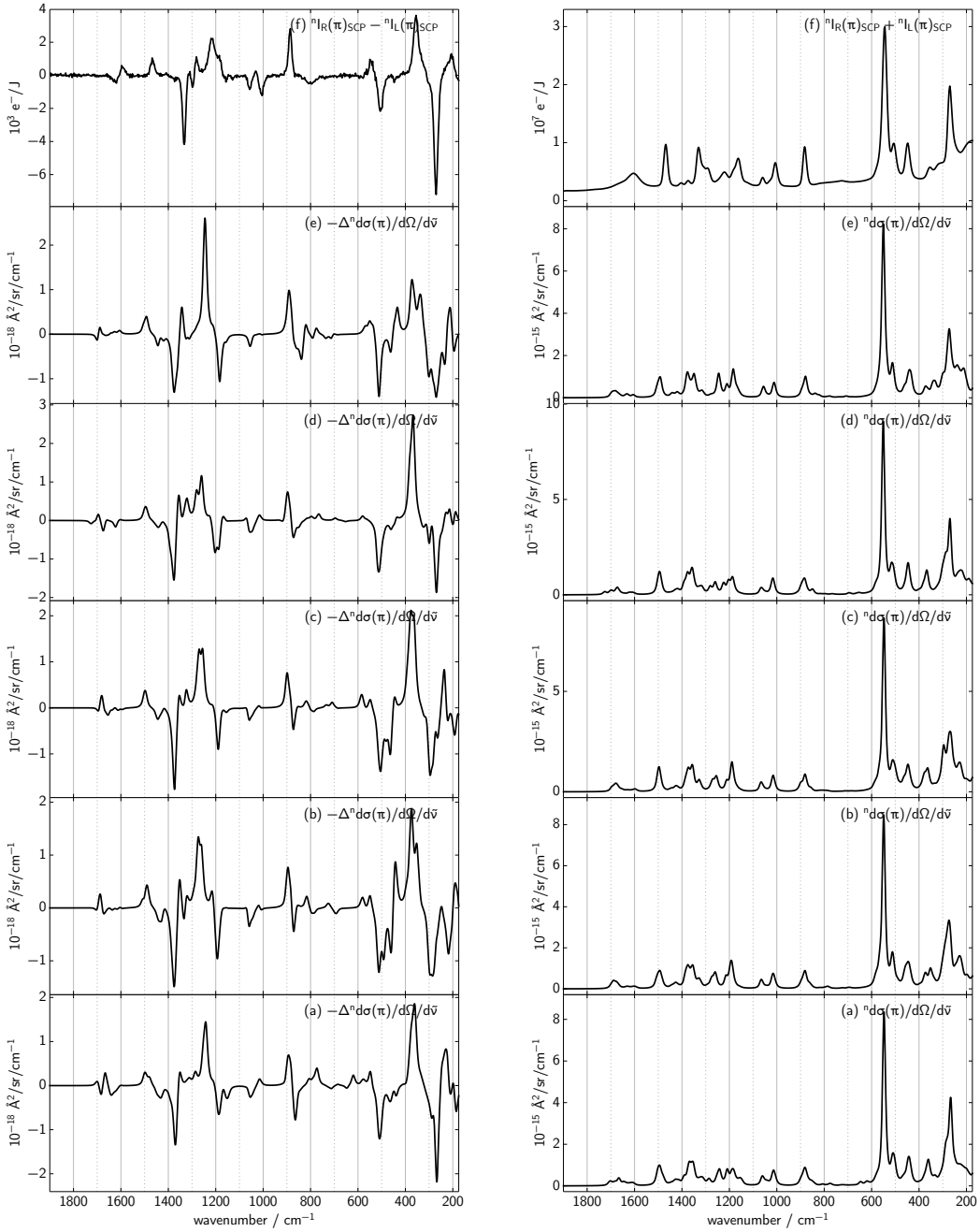


Figure 9 (1/3) ROA (*left*) and Raman (*right*) spectra – comparison of the mean theoretical spectra for the 5 BOMD snapshots of $\Lambda(\delta\delta\delta)$−$[Rh(en)_3]^{3+}$ with its first solvation sphere (a–e) with the experiment (f). Snapshots taken at 0.0 ps (a), 2.5 ps (b), 5.0 ps (c), 7.5 ps (d), and 10.0 ps (e)

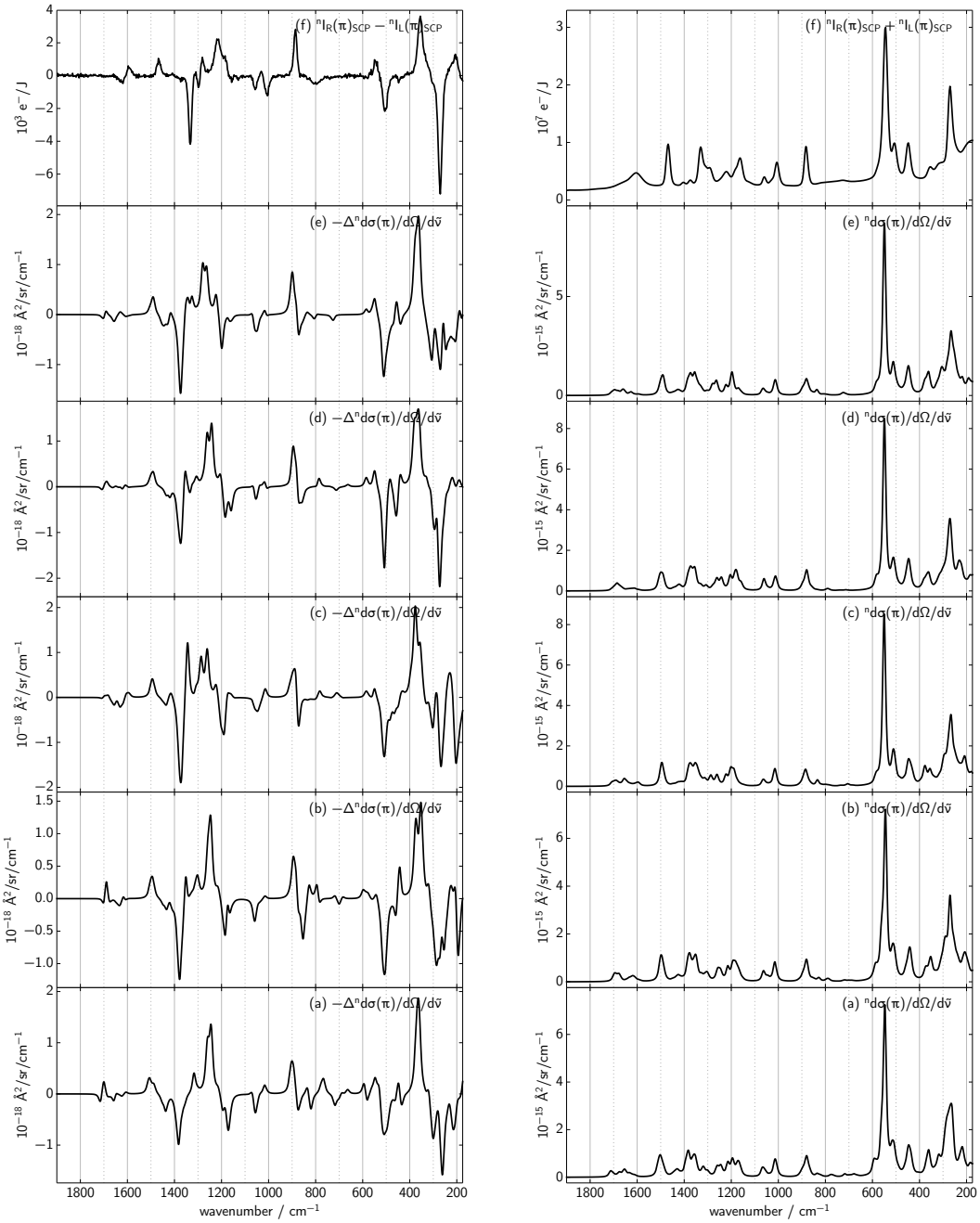


Figure 9 (2/3) ROA (*left*) and Raman (*right*) spectra – comparison of the mean theoretical spectra for the 5 BOMD snapshots of $\Lambda(\delta\delta\delta)$−[Rh(en)$_3$]$^{3+}$ with its first solvation sphere (a–e) with the experiment (f). Snapshots taken at 12.5 ps (a), 15.0 ps (b), 17.5 ps (c), 20.0 ps (d), and 22.5 ps (e)

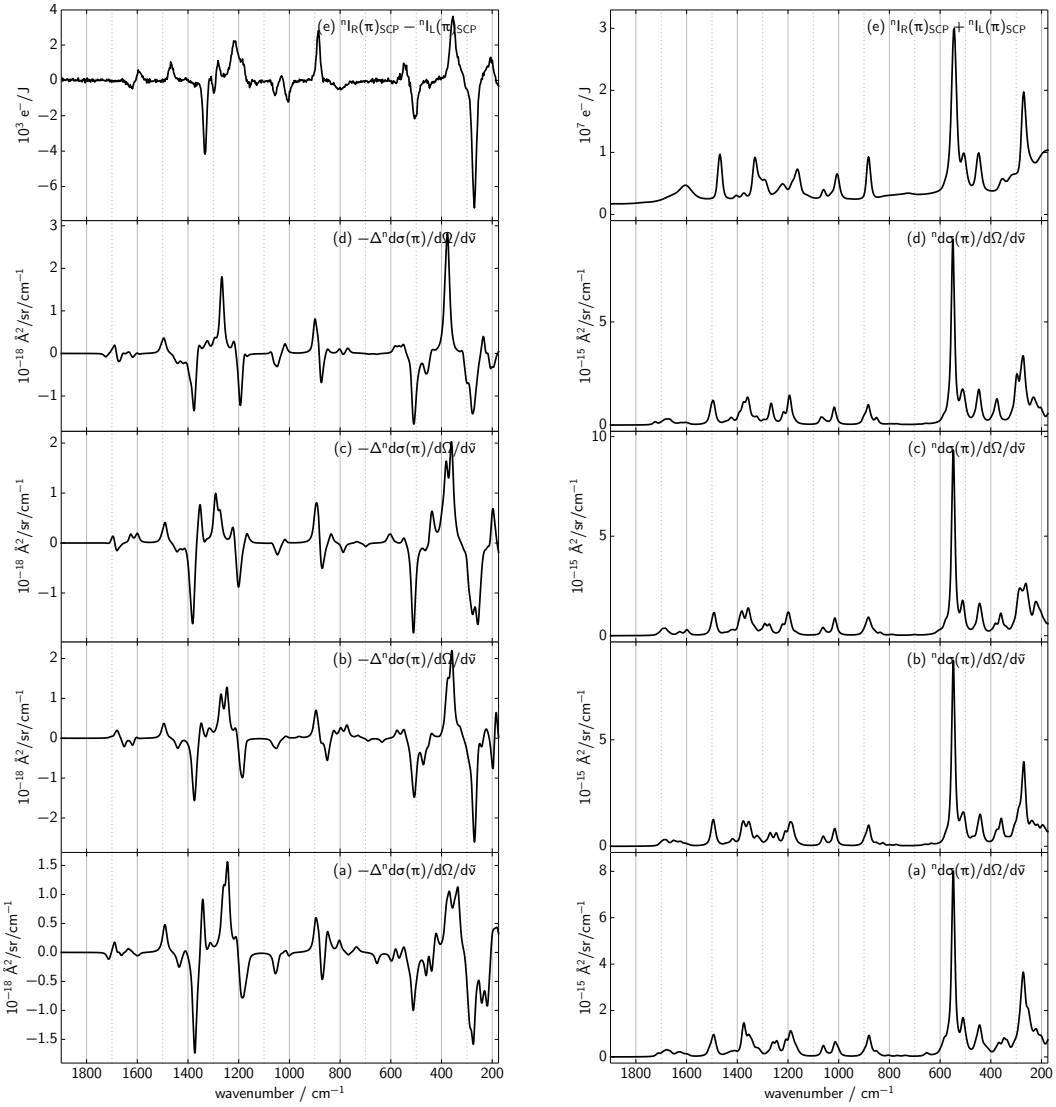


Figure 9 (3/3) ROA (*left*) and Raman (*right*) spectra – comparison of the mean theoretical spectra for the 4 BOMD snapshots of $\Lambda(\delta\delta\delta)$−[Rh(en)$_3$]$^{3+}$ with its first solvation sphere (a–d) with the experiment (e). Snapshots taken at 25.0 ps (a), 27.5 ps (b), 30.0 ps (c), and 32.5 ps (d)

Table 7 Total energies (E) in Hartree and their weights (w) of the four different conformers of the *tris*(ethylenediamine)rhodium(III) complex of the Λ configuration. Theoretical level: B3LYP (neither solvation model, nor dispersion used) for three different basis sets. The subscripts stand for the basis sets TZVP (a), def2-TZVP (b), and def2-TZVPD (c). The superscripts indicate SCF electronic energies (1), and the sum of electronic and thermal free energies as implemented in Gaussian 09 C.01 (2). Weights (w) are calculated from Boltzmann distributions at 298K.

	Λ($\lambda\lambda\lambda$)	Λ($\lambda\lambda\delta$)	Λ($\lambda\delta\delta$)	Λ($\delta\delta\delta$)
E_a^1	-681.03408	-681.03411	-681.03345	-681.03322
w_a	33.86%	34.99%	17.46%	13.69%
E_b^1	-681.55252	-681.55252	-681.55196	-681.55169
w_b	33.82%	33.66%	18.54%	13.97%
E_c^1	-681.55522	-681.55521	-681.55465	-681.55440
w_c	33.87%	33.39%	18.49%	14.25%
E_a^2	-680.72030	-680.71994	-680.71966	-680.72012
w_a	33.20%	22.61%	16.75%	27.44%
E_b^2	-681.23976	-681.23932	-681.23861	-681.23976
w_b	34.28%	21.44%	10.15%	34.13%
E_c^2	-681.24276	-681.24233	-681.24163	-681.24278
w_c	33.86%	21.41%	10.18%	34.55%

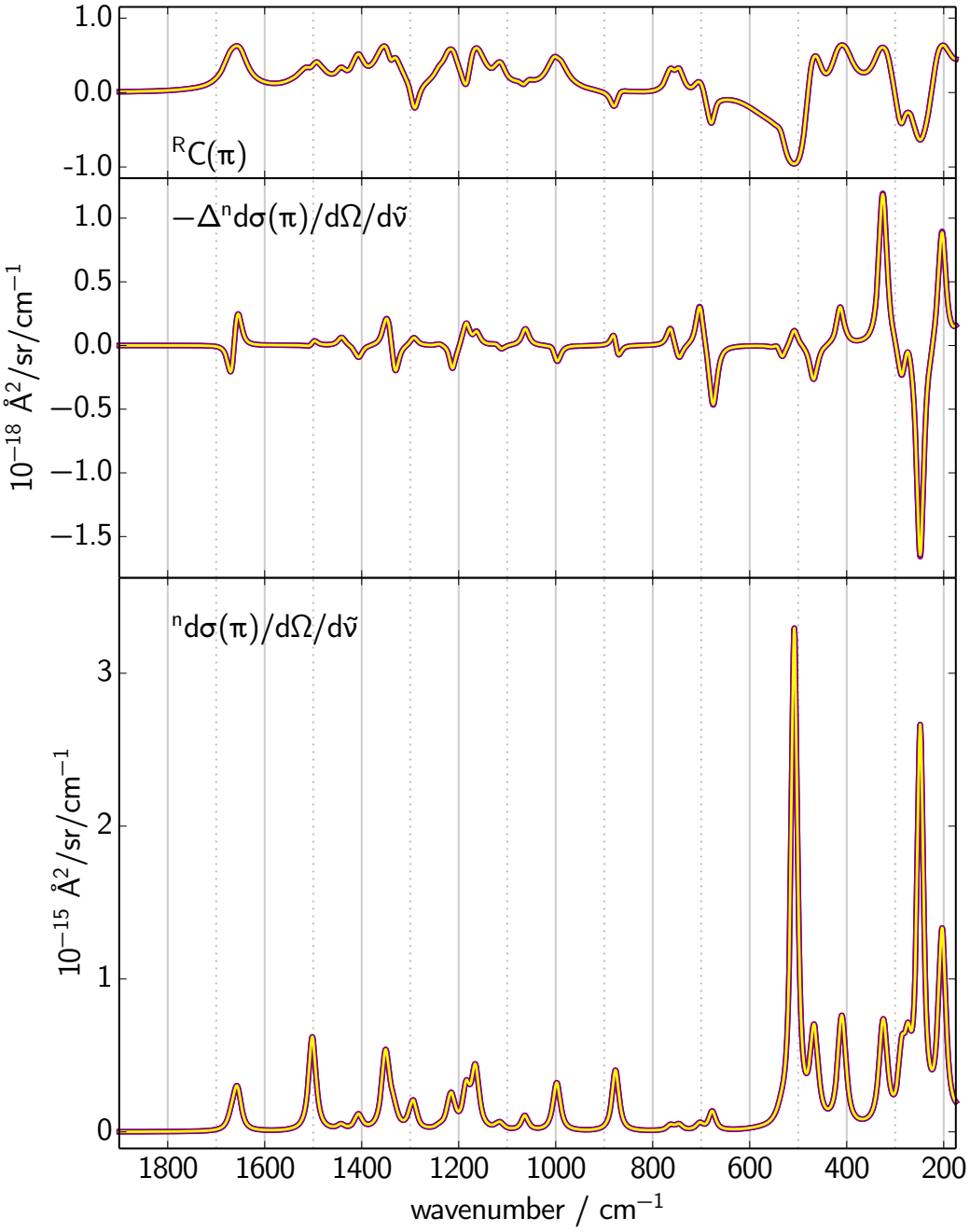


Figure 10 Raman, ROA, and degree of circularity spectra (*bottom* to *top*) of the calculated spectra of $\Lambda(\lambda\lambda\delta)$ conformer. B3LYP/def2-TZVP. Comparison of results obtained with Gaussian 09 Revision C01 (purple outline) and Revision D01 (yellow line).