Supplementary Material for PCCP

Supporting Information

Formation and Structure of the Potassium Complex of Valinomycin in Solution Studied by the Raman Optical Activity Spectroscopy

Shigeki Yamamoto, Michal Straka, Hitoshi Watarai, and Petr Bouř

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Table S1. Vibrational assignment of most intense Raman peaks in the K^+-valinomycin complex, based on the BP86/SVP computation.

BP86	BPW91/6-31G**	BPW91/6-31G**/CPCM	B3LYP/6-31++G**/CPCM	Exp	assignment
1745	1776	1740	1771	1757	ν(C=O), ester, sym.
1686	1676	1662	1688	1661	ν(C=O), amide
1656	1665	1643	1671	1646	ν(C=O), amide, sym.
1520	1578	-	1567	1535	Amide II (δ(NH))
1446	1525	1470	1502	1468	$\delta(CH_3)$, asym
1427	1508	1455	1487	1447	
1375			1408	1395	$\delta(CH_3)$, sym
1357	1423		1403	1376	
1332	1398		1382	1352	$\delta(C_\alpha H) + \delta(C_\beta H)$
1294	1358	1285	1331	1313	$\delta(NH) + \delta(C_\alpha H) + \delta(C_\beta H)$
	1316	1262	1300	1266	$\delta(C_\alpha H) + \delta(C_\beta H)$
	1302	1238	1283	1249	Amide III (δ(NH), i.p.)
1179	1219	1173	1215	1192	
1156		1140	1170	1154	isopropyl
1116	1159	1114	1144	1128	
			1144 1107	1098	Amide + isopropyl
			1034	1045	
			1014	1020	
			982	981	
			968	962	$\rho(CH_3)$, isopropyl
924			944	941	
871			886	887	
			868	865	
			844	841	
			791	792	Amide V (δ(NH), oop)
727		716	745	745	Amide VI (δ(COO), oop.) + CH_3
		669	683	673	
		650	663	652	Amide VI (δ(COO), o.p.) + CH_3
		629	652	638	
		611	634	629	
478	499	470	487	491	All atom without COO
401	417	396	410	408	isopropyl + COO
338	352	334	345	345	Amide V (δ(NH), o.p.) + isopropyl
	330	308	321	321	Ring breathing
			219	224	$\tau(CH_3)$
RMS: 15	32	15	22	0	

Table S2. Calculated relative energies of all C_3 symmetric K^+-valinomycin complex conformers

	AM1	PM3	HF/3-21G	BPW91/6-31G**	vdW-BPW916-31G**	BPW91/6-31G**/cpcm	B3LYP/6-31G**	vdW-HF/3-21G
s1	7.9	5.9	19.2	22.9	13.2	19.5	17.5	14.5
s2	8.4	11.8	18.8	25.5	11.6	21.8	19.0	13.1
s3	7.7	8.0	18.1	20.2	13.6	22.0	19.3	15.8
s4	10.1	12.0	18.0	21.0	14.1	19.6	19.9	15.3
s5	8.9	5.6	18.5	23.4	11.2	20.1	18.6	12.2
s6	9.6	11.0	18.8	25.2	12.5	18.3	19.7	13.7
s7	4.4	7.5	9.1	11.7	4.4	11.3	10.5	1.7
s8	4.0	2.0	9.2	9.0	4.3	9.5	9.0	2.6
s9	4.2	8.0	7.6	11.9	5.9	11.7	10.7	3.3
s10	7.3	11.5	17.3	23.5	12.8	14.8	16.0	15.1
s11	13.3	13.2	26.4	18.4	14.9	20.8	19.3	11.1
s12	14.4	13.9	20.5	18.7	15.7	22.3	19.6	18.6
s13	8.4	11.0	18.0	15.8	10.9	19.0	16.8	12.7
s14	13.4	12.8	20.3	19.2	14.5	21.4	19.8	15.8
s15	9.1	12.8	20.2	19.7	16.8	21.9	20.4	18.2
s16	3.1	6.2	8.0	9.4	6.9	11.0	7.7	7.2
s17	2.9	6.6	10.1	10.4	6.8	9.4	10.4	5.3
s18	3.2	8.7	10.2	10.5	8.3	11.1	10.7	7.3
s19	2.3	4.9	9.8	7.8	6.0	8.7	8.3	3.7
s20	3.2	5.8	10.1	10.2	7.5	10.6	10.2	8.6
s21	3.7	5.4	12.0	11.8	10.2	14.0	11.8	16.9
s22	0.9	0.5	1.0	2.3	1.0	1.9	2.0	4.6
s23	4.0	5.3	7.2	8.9	3.4	9.8	8.9	0.0
s24	4.8	6.2	10.6	11.1	5.7	12.2	11.5	14.5
s25	4.8	5.2	12.6	13.0	11.5	11.5	12.6	17.6
s26	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.6
s27	0.6	0.8	2.5	3.7	3.5	3.0	3.4	7.1

Table S3. Calculated equilibrium side chain torsional angles in the 27 C_3-symmetric conformations of the K^+-valinomycin complex

	HF/3-21G			BPW91/6-31G**		
Conformer	D-Val	L-Val	D-Hiv	D-Val	L-Val	D-Hiv
s1	56	66	64	56	70	63
s2	51	79	-65	51	77	-64
s3	50	78	176	51	75	-177
s4	-74	77	176	-73	75	-178
s5	-77	75	67	-76	73	62
s6	-72	78	-63	-72	76	-64
s7	-177	77	-63	-178	75	-63
s8	-178	77	64	-178	76	64
s9	-176	76	176	-179	74	179
s10	56	-53	64	56	-53	63
s11	52	-51	-65	53	-52	-66
s12	53	-55	178	53	-56	-177
s13	-77	-50	63	-74	-50	62
s14	-66	-56	-63	-67	-57	-64
s15	-69	-56	178	-66	-56	177
s16	-179	-58	64	-178	-56	62
s17	180	-62	-58	180	-58	-62
s18	-177	-57	180	180	-57	180
s19	58	175	62	58	180	63
s20	53	176	-69	53	177	-69
s21	48	178	177	49	178	180
s22	179	177	-65	-178	163	-66
s23	-76	174	61	-75	179	63
s24	-72	178	-68	-77	178	-69
s25	-74	177	176	-73	176	179
s26	-179	179	64	-178	178	63
s27	-177	177	176	-178	178	179

Table S4. Twelve AM1 lowest energy conformers, calculated isopropyl torsional angles, relative energies, and Boltzmann populations (C_3 symmetric conformers are on the red background)

a) Torsional angles (BPW91/6-31G**)

Conf.	D-Val	L-Val	D-Hiv	D-Val	L-Val	D-Hiv	D-Val	L-Val	D-Hiv
1	-173	173	66	-173	173	66	-173	173	66
2	-173	173	66	-173	173	65	-173	173	-178
3	-173	173	66	-172	173	-67	-173	173	66
4	-173	173	-179	-173	173	65	-173	173	-178
5	-173	173	66	-172	173	-67	-173	173	-178
6	-173	173	-67	-172	172	-67	-173	173	66
7	-173	173	-179	-173	172	-67	-174	173	66
8	-173	173	-179	-173	172	-178	-173	173	-178
9	-173	172	-67	-173	172	-178	-173	173	-178
10	-173	172	-67	-172	172	-67	-173	173	-67
11	-173	172	-67	-172	172	-67	-173	173	-178
12	-173	174	66	-173	173	66	57	173	67

b) Relative energies

Conf.	AM1	PM3	bpw91 6-31G**	bpw91[a] 6-31G**	B3LYP 6-31G**	B3LYP 6-311++G**	population Cal.[c]	population Exp.[d]
1	0.0	0.0	*0.0*	*0.0*	*0.0*	*0.0*	*28*	*39*
2	0.2	0.4	*1.4*	*1.3*	*1.2*	*1.6*	*9*	
3	0.2	0.2	*0.8*	*0.6*	*0.7*	*0.9*	*29*	*43*
4	0.4	0.6	*2.6*	*2.2*			*2*	
5	0.4	0.5	*2.2*	*1.7*			*5*	
6	0.5	0.4	*1.5*	*1.1*	*1.5*	*1.6*	*14*	*18*
7	0.5	0.5	*2.1*	*1.6*			*6*	
8	0.5	0.9	*3.8*	*3.0*			*0*	
9	0.7	0.8	*3.3*	*2.5*			*1*	
10	0.7	0.5	*2.3*	*1.7*			*2*	
11	0.7	0.6	*2.9*	*2.2*			*2*	
12	0.8	1.2	*3.6*	*2.7*			*1*	

[a] CPCM(methanol) solvent correction

[c] based on the BPW91/6-31G**/CPCM(methanol) energies

[d] based on the ROA spectral decomposition

Table S5. Functional performance comparison. For the L-Lac-L-Val-D-Hiv-D-Val-K^+ fragment, torsion angles constrained to mimic valinomycin complex, CPCM model with MeOH, 6-311++G** basis set. See also Figure S6.

functional	Δ_{RAM}	Δ_{FREQ}	**s**	**t** [days]
B3LYP	0.25	16	1.015	6.3
M5	0.28	34	1.034	7.5
M06	0.25	24	1.024	8.4
M06L	0.28	22	1.022	6.8
M062X	0.32	37	1.037	11.5
B3PW91	0.27	21	1.022	8.9

Δ_{RAM} - RMS error of calculated Raman spectral intensities, against normalized experimental spectrum

Δ_{FREQ} - average absolute deviation against selected experimental (408, 745, 1129, 1315, 1450, 1647 and 1756 cm^{-1}) frequencies

s - slope of a linear fit to the experimental frequencies

t - time of the frequency (with the Raman and ROA options) Gaussian calculation, per one Intel Xeon E5530 CPU at 2.40GHz

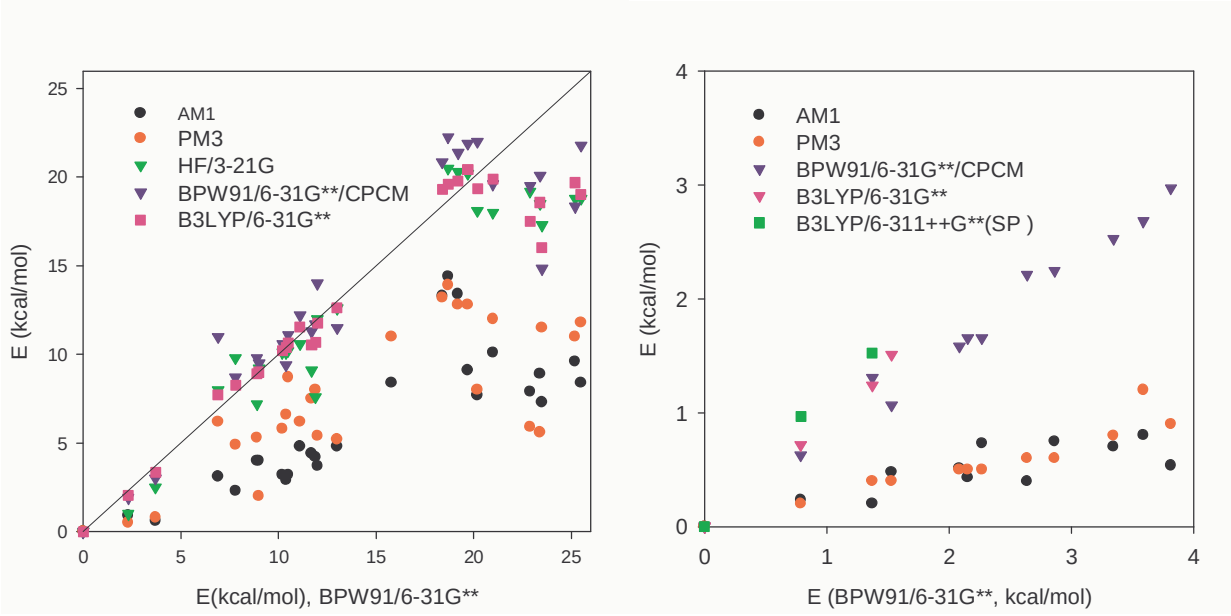

Figure S1. Relative energies of the (left) 27 symmetric (C_3) and (right) 12 lowest-AM1 energy valinomycin.K^+ conformers calculated at different approximation levels. For the AM1 and PM3 methods a pseudo-atom was used instead of K^+ as described in the text.

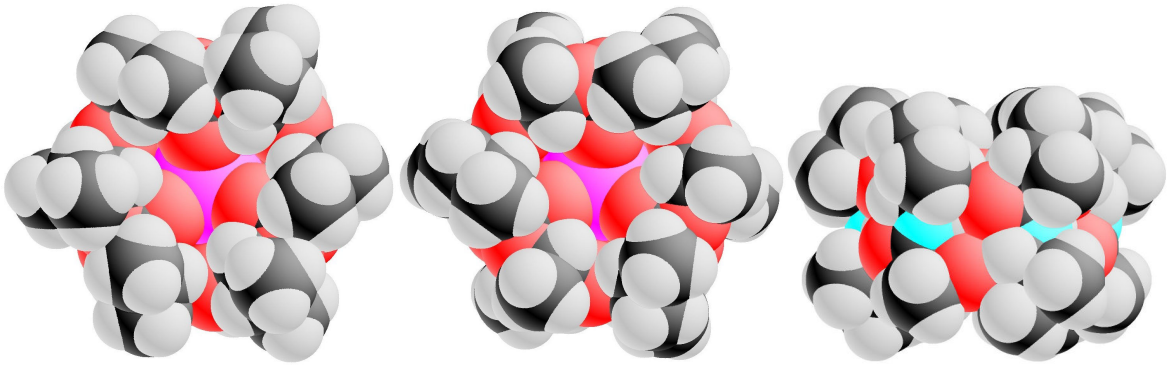

Figure S2. Lowest-energy conformation (BPW91/6-31G**/CPCM(MeOH)) of the potassium-valinomycin complex, top, bottom and side view.

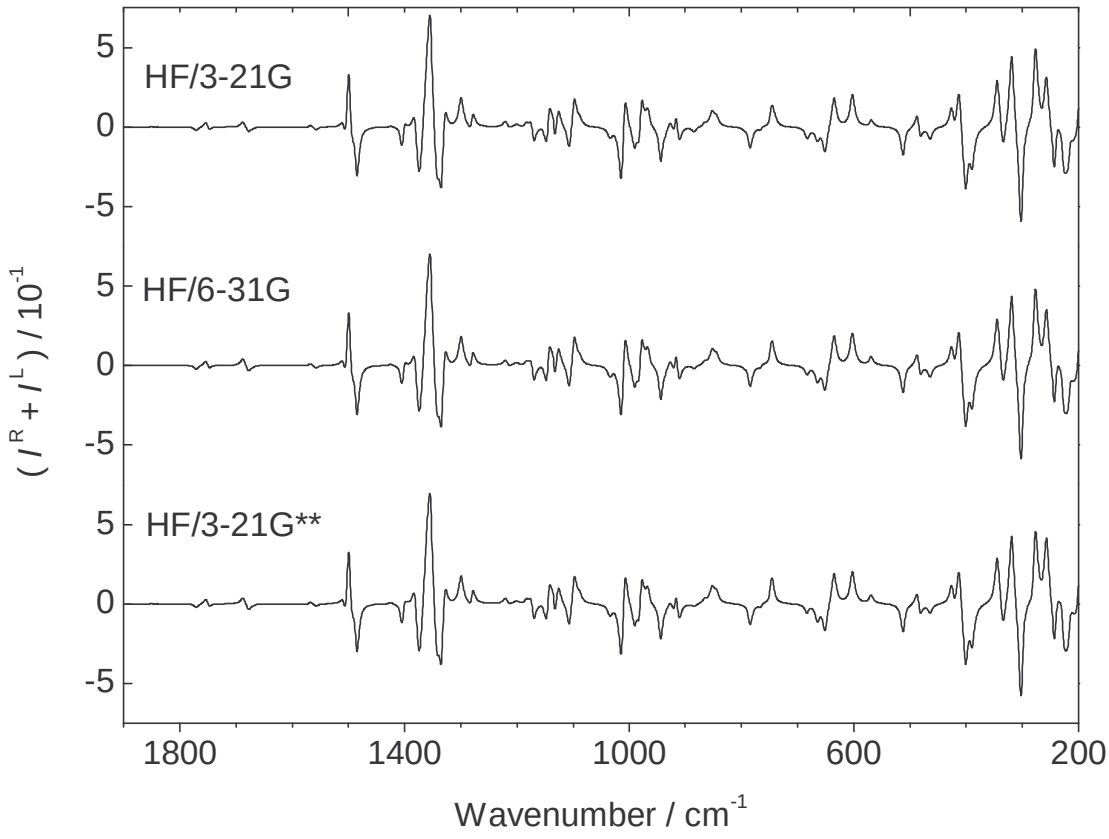

Figure S3. ROA complex spectra simulated with the local G' and A tensor parts at the HF/3-21G, HF/6-31G and HF/6-31G** levels, with the B3LYP/6-31++G**/CPCM force field and Raman polarizability.

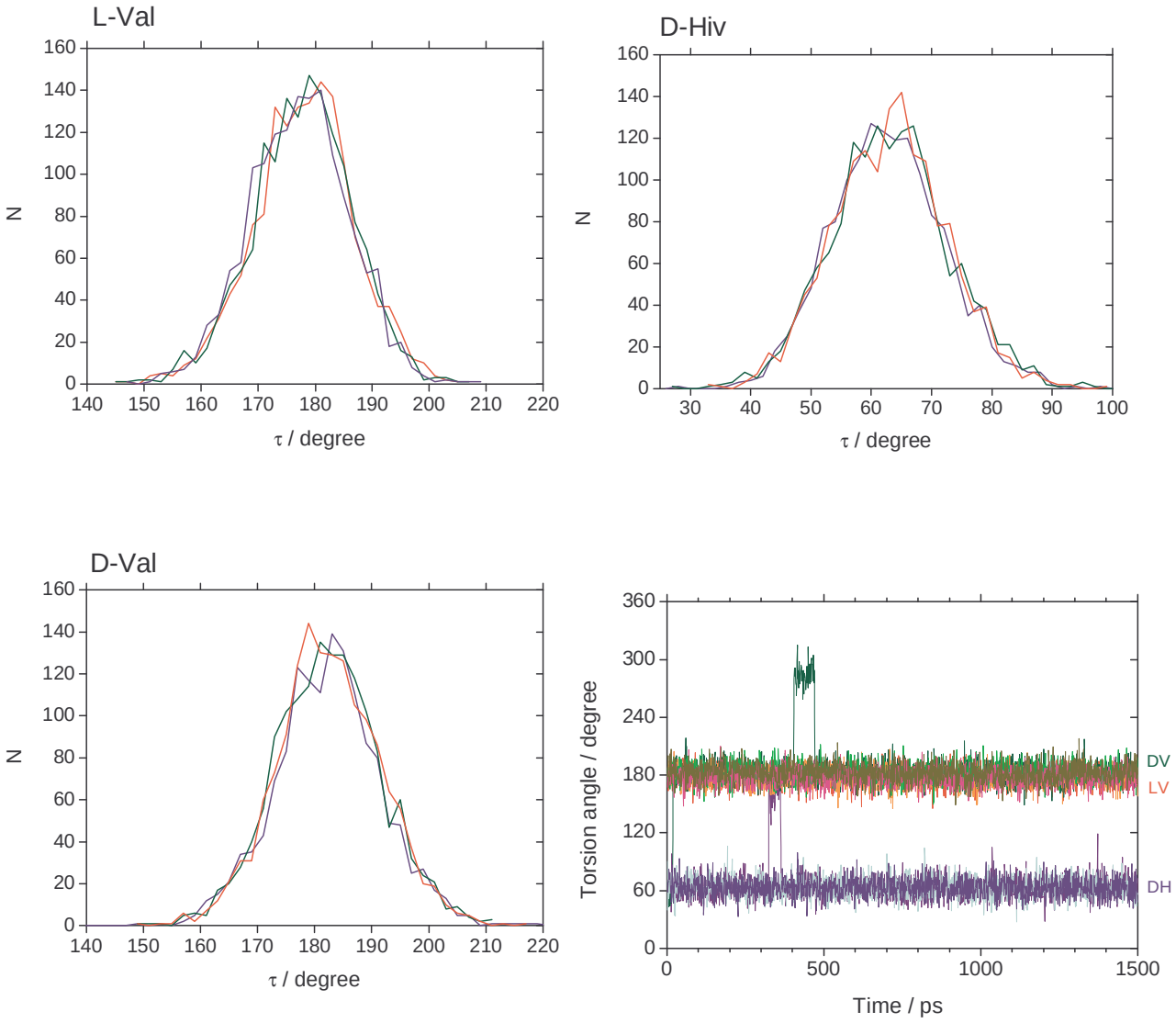

Figure S4. Distribution of the isopropyl torsional angles obtained from the MD simulations, and their time development(L-Val: red, D-Hiv: blue, D-Val: green) during a 1.5 ns run.

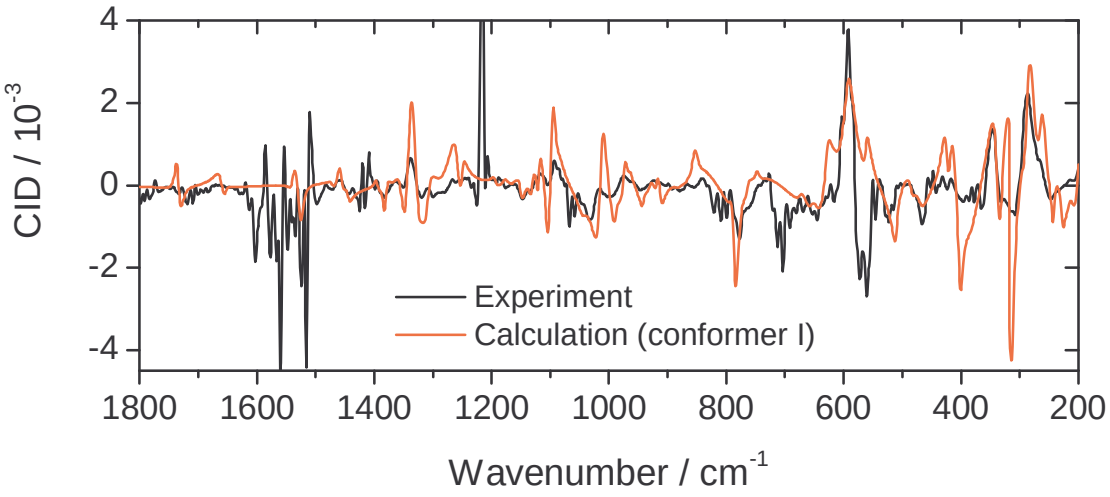

Figure S5. Experimental and calculated CID=$(I^R-I^L)/(I^R+I^L)$ ratios obtained by a direct division of the ROA and Raman spectra.

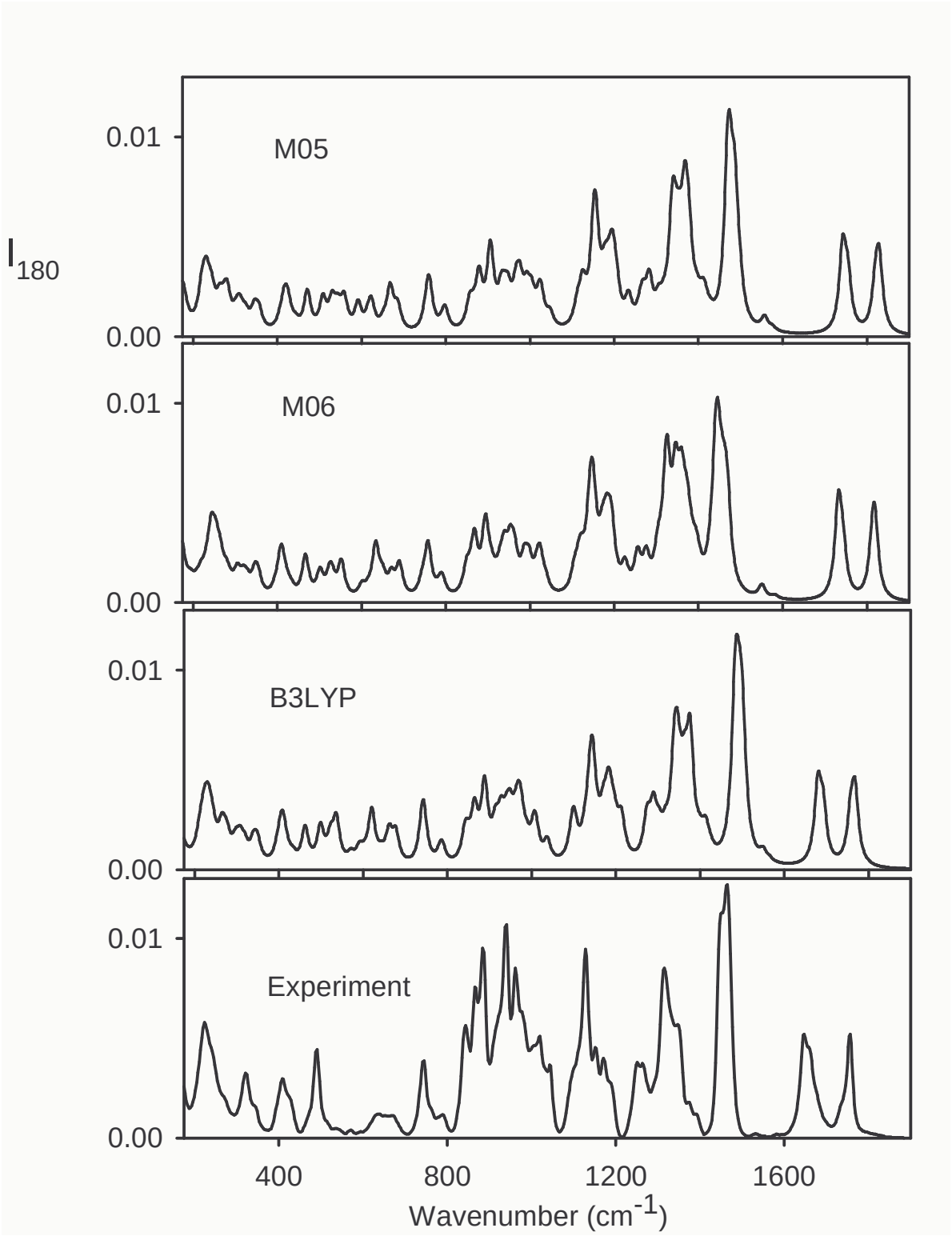

Figure S6. Raman spectra of the L-Lac-L-Val-D-Hiv-D-Val-K^+ model fragment calculated with several functionals (6-311++G** basis, CPCM(MeOH), and the valinomicin complex spectrum. See also Table S5.

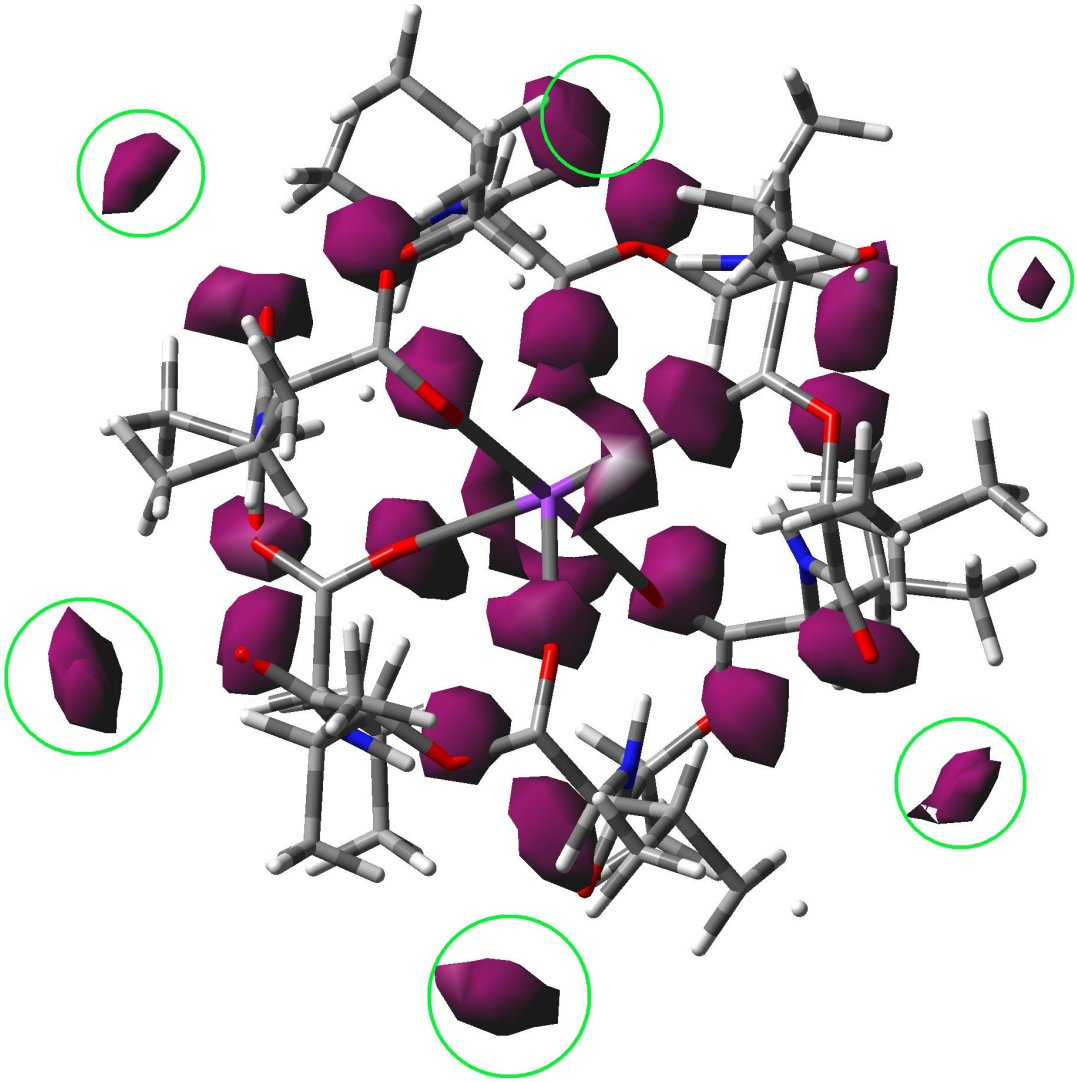

Figure S7. Oxygen probability distribution (methanol oxygens in green circles, first hydration sphere included only) obtained for the valinomycin complex soaked in methanol. The distribution is based on MD computation, periodic $(30Å)^3$ box, NVT ensemble, 1 fs integration step, 1.5 ns simulation (sampled at 1 ps intervals), Amber 99 force field[1] and the Tinker software.[2]

1. J. Wang, P. Cieplak and P. A. Kollman, *J. Comput. Chem.*, 2000, **21**, 1049-1074.
2. J. W. Ponder, Washington University School of Medicine, Saint Louis, 3.8 edn., 2000.

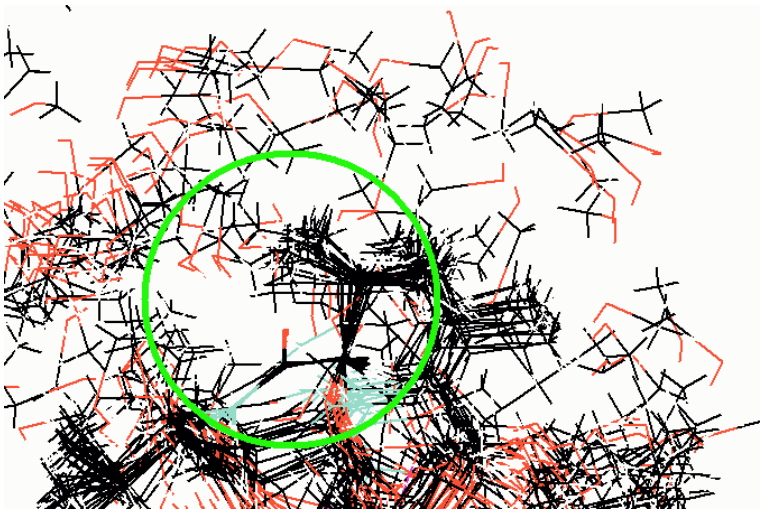

Figure S8. Twenty random MD snapshots (MD parameters are listed in caption of Figure S7) of the valinomycin complex and methanol molecules closest to the amide group within the green circle.

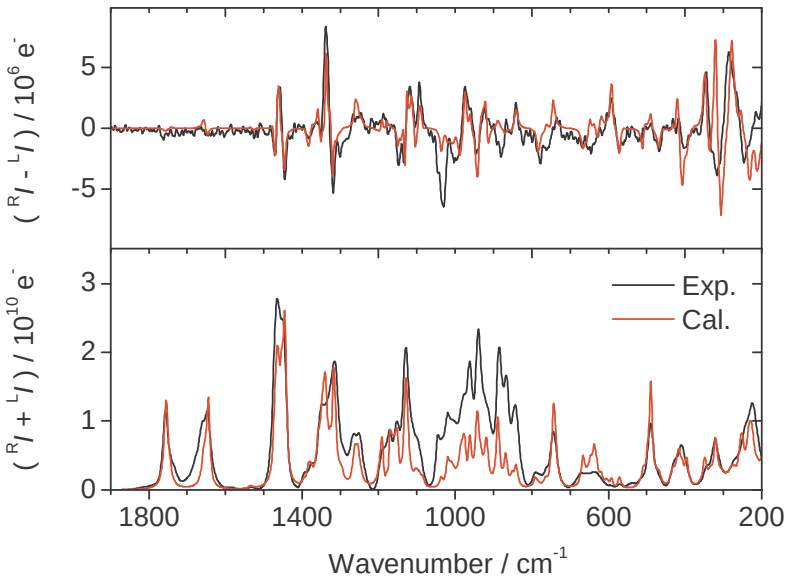

Figure S9. The fitted (red, based on the B3BPW91/6-31++G**/CPCM(MeOH)/HF/6-31G** conformer subspectra) and experimental (black) ROA (top) and Raman (bottom) spectra of the K^{+}-valinomycin complex.