Electronic Supplementary Material (ESI) for CrystEngComm

ELECTRONIC SUPPLEMENTARY INFORMATION

Silver (II) triflate with one dimensional $[Ag(II)(SO_3CF_3)_{4/2}]_\infty$ chains hosting antiferromagnetism

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S1. Reproduction of the unit cell parameters, the Ag–O bond lengths, and of the Ag–O–O angles with various spin–nonpolarized periodic calculations for Z=1 unit cell.

	Exp	LDA	GGA (PBE)	GGA (PBEsol)	HSE06 (PBEsol)
a (Å)	4.9117	4.783	5.057	4.964	4.909
Δa_exp(%)		*-2.6*	*3.0*	*1.1*	*0.0*
b (Å)	5.1136	4.885	5.373	5.219	5.160
Δb_exp(%)		*-4.5*	*5.1*	*2.1*	*0.9*
c (Å)	11.033	10.689	11.339	11.195	11.033
Δc_exp(%)		*-3.1*	*2.8*	*1.5*	*0.0*
α (°)	80.0	80.6	80.8	80.4	80.5
Δα_exp(%)		*0.8*	*1.1*	*0.6*	*0.7*
β (°)	75.8	76.2	77.2	76.6	76.9
Δβ _exp(%)		*0.6*	*1.8*	*1.1*	*1.5*
γ (°)	61.6	60.7	11.3	61.3	61.4
Δγ_exp(%)		*-1.4*	*-81.6*	*-0.4*	*-0.3*
V(Å^3)	235.7	211.3	262.9	247.0	238.5
ΔV_exp(%)		*-10.4*	*11.5*	*4.8*	*1.2*
d(Ag-O)1	2.07	2.136	2.223	2.175	2.154
d1%		*2.9*	*7.1*	*4.8*	*3.8*
d(Ag-O)2	2.09	2.141	2.232	2.184	2.164
d2%		*2.2*	*6.6*	*4.3*	*3.3*
d(Ag-O)3	2.49	2.455	2.66	2.56	2.548
d3%		*-1.4*	*6.8*	*2.8*	*2.3*
Ag-O-O (°)	98.1	93.17	97.5	96.5	96.9
O-O-Ag (°)	140.5	135.4	139.1	138.4	138.9

S2. Reproduction of the unit cell parameters, the Ag–O bond lengths, and of the Ag–O–O angles with spin–polarized DFT calculations for Z=4 (2x2x1) magnetic cell.

	Exp	Spin-polarized GGA-PBEsol	Spin-polarized +U GGA-PBEsol
a (Å)	4.9117	4.9285	4.935
Δa_exp(%)		*0.3*	*0.5*
b (Å)	5.1136	5.187	5.185
Δb_exp(%)		*1.4*	*1.4*
c (Å)	11.033	11.135	11.103
Δc_exp(%)		*0.9*	*0.6*
α (°)	80.0	80.1	80.2
Δα_exp(%)		*0.2*	*0.3*
β (°)	75.8	76.9	76.3
Δβ _exp(%)		*1.5*	*0.7*
γ (°)	61.6	61.3	61.4
Δγ_exp(%)		*-0.4*	*-0.3*
V (Å^3)	235.7	242.6	241.9
ΔV_exp(%)		*2.9*	*2.6*
d(Ag-O)1	2.07	2.183	2.153
d1%		*5.2*	*3.8*
d(Ag-O)2	2.09	2.188	2.158
d2%		*4.5*	*3.1*
d(Ag-O)3	2.49	2.522	2.532
d3%		*1.3*	*1.7*
Ag-O-O (°)	98.1	94.9	97.4
O-O-Ag (°)	140.5	138.6	138.4

S3. Single-point free energies and resulting magnetic-exchange J parameters calculated at GGA-PBEsol+U level for five different spin-ordering schemes using the 2x2x1 magnetic supercell: (I.) magnetic excitations from non-spin polarized ground state, (II.) magnetic excitations from spin-polarized AFM-fm+U ground state – for geometry see Table 2).

Ordering (intra_inter-chain)	E per FU	I.	II.
non-mag	E_0 / eV	-71.17532	-71.15828
AFM_fm	E_1	**-71.35886**	**-71.36272**
AFM_afm	E_2	-71.35872	-71.36257
FM_fm	E_3	-71.32255	-71.32930
FM_afm	E_4	-71.32106	-71.32809
	J_{12} / meV	-0.14	-0.15
	J_{13}	-36.30	-33.42
	J_{14}	-37.79	-34.63
	J_{24}	-37.66	-34.48
	J_{34}	-1.49	-1.21

Assuming weak inter-chain coupling (which is the case), the value of $J_{inter\text{-}chain}$ can be approximated as J_{24} or alternatively J_{13}, consistently yielding $J_{intra\text{-}chain}$ of –33.4 to –34.5 meV. An estimate of $J_{inter\text{-}chain}$ is more difficult, as the superexchange pathway is more complex, but from $-J_{12}$ or alternatively $-J_{34}$ one gets +0.15 to +1.2 meV (here, negative sign corresponds to a preferred AFM and positive sign to FM coupling). In any case, $|J_{inter\text{-}chain}| / |J_{intra\text{-}chain}|$ ratio is of the order of $\sim 4\times10^{-3}$–4×10^{-2} which reconfirms pronounced 1D character of magnetism.

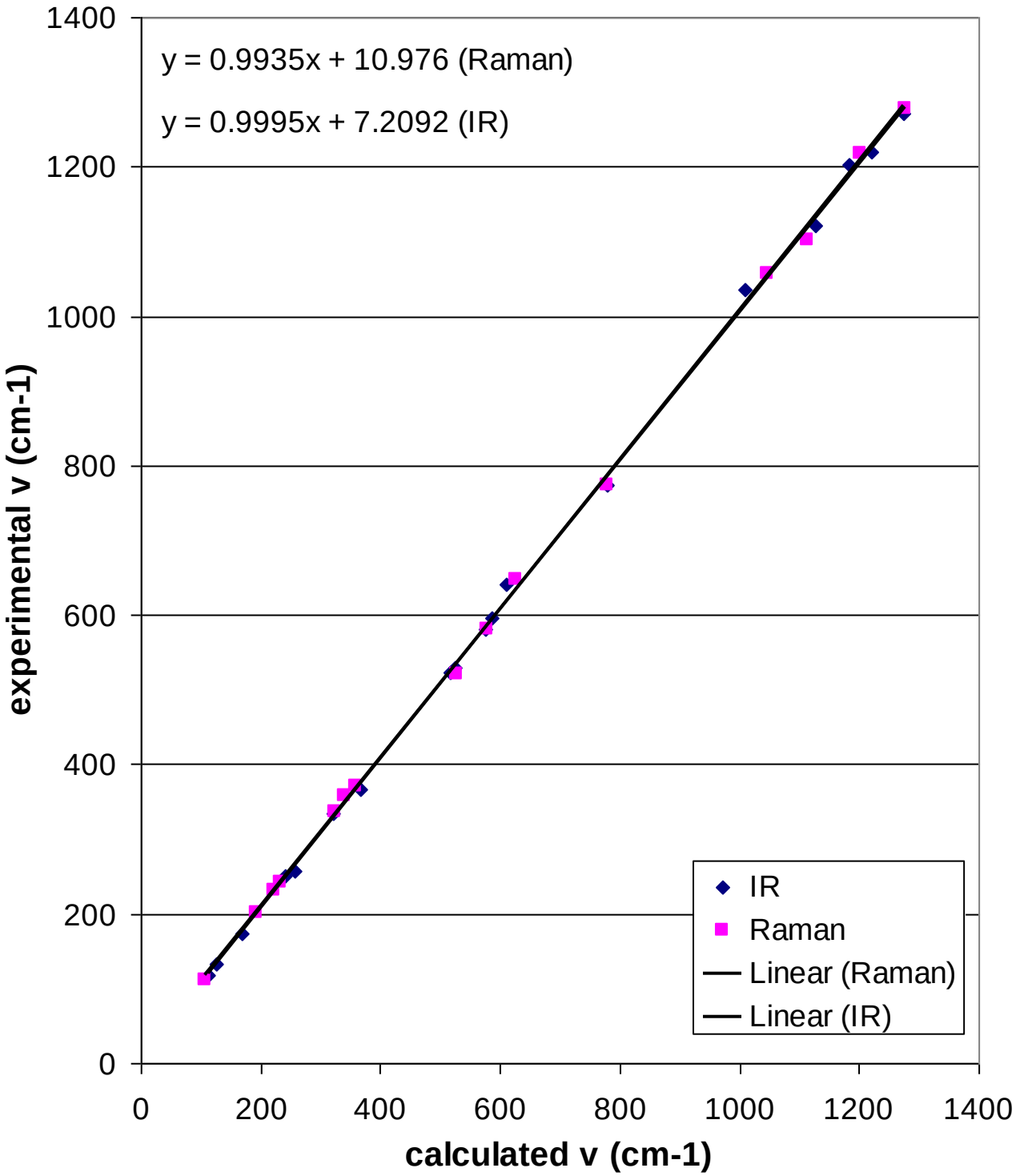
S4. The calculated phonon frequencies at Γ for $Ag(OTf)_2$ as compared to experimental IR absorption and Raman spectra.*

IR**		Raman**	
1272	1275	1278	1277
1219	1220	1217	1202
1202	1184	**1103**	1113
1122	1127	1058	1047
1035	1009	774	779
773	778	648	626
641	610	582	578
595	585	520	527
580	575	**370**	358
529	526	357	340
523	516	337	323
367	368	**242**	233
334	321	231	221
258	257	**202**	193
250	240	112	107
174	168		
132	127		
117	113		

* Scaling factor of 1.06 has been used for calculated frequencies to account for the fact that the method slightly underestimated the volume of the unit cell and the strength of chemical bonds.

** Very strong and strong modes predominating the spectra, have been marked in bold fonts.

S5. Linear regressions between the calculated phonon frequencies at Γ* for $Ag(OTf)_2$ and the experimental frequencies (separately for IR absorption and Raman spectra).**



* scaled (x1.06)

** The regressions for IR and Raman spectra have nearly identical (and close to unity) linear coefficients and constants, and excellent R^2 of 0.9994 and 0.9995, respectively.