

Assessing Cluster Models of Solvation for the Description of Vibrational Circular Dichroism Spectra: Synergy between Static and Dynamic Approaches

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Supplementary Information

	ΔG	E_0	$E_0 + ZPE$
bi-eqg ⁺ G ⁻	0.0	0.0	0.0
mono _{OH} -eqg ⁻ G ⁻	1.4	3.3	2.0
mono _{OH} -eqg ⁻ G ⁺	2.0	5.3	4.3
mono _{OH} -eqtG ⁻	2.4	3.9	3.3
mono _{OH} -eqg ⁻ T	3.4	6.2	5.0
noHB-eqg ⁺ G ⁺	3.4	26.4	22.9
bi-eqg ⁺ T	4.1	3.1	2.9
mono _{OH} -axg ⁺ T	4.7	9.4	8.2
mono _{OH} -eqtT	6.8	7.7	7.4
mono _{NH} -eqg ⁺ G ⁺	10.8	17.6	15.8
mono _{OH} -eqg ⁺ G ⁺	12.7	4.0	3.5
mono _{OH} -axtG ⁻	13.7	11.9	11.7
mono _{OH} -axtT	16.2	15.2	14.5

Table S1: Comparison between Gibbs free energies ΔG at room temperature, electronic energies E_0 at 0K, and ZPE-corrected electronic energies at 0K (kJ/mol) $E_0 + ZPE$, for the most stable 1-1 complexes calculated at the B3LYP/6-311++G(d,p) level.

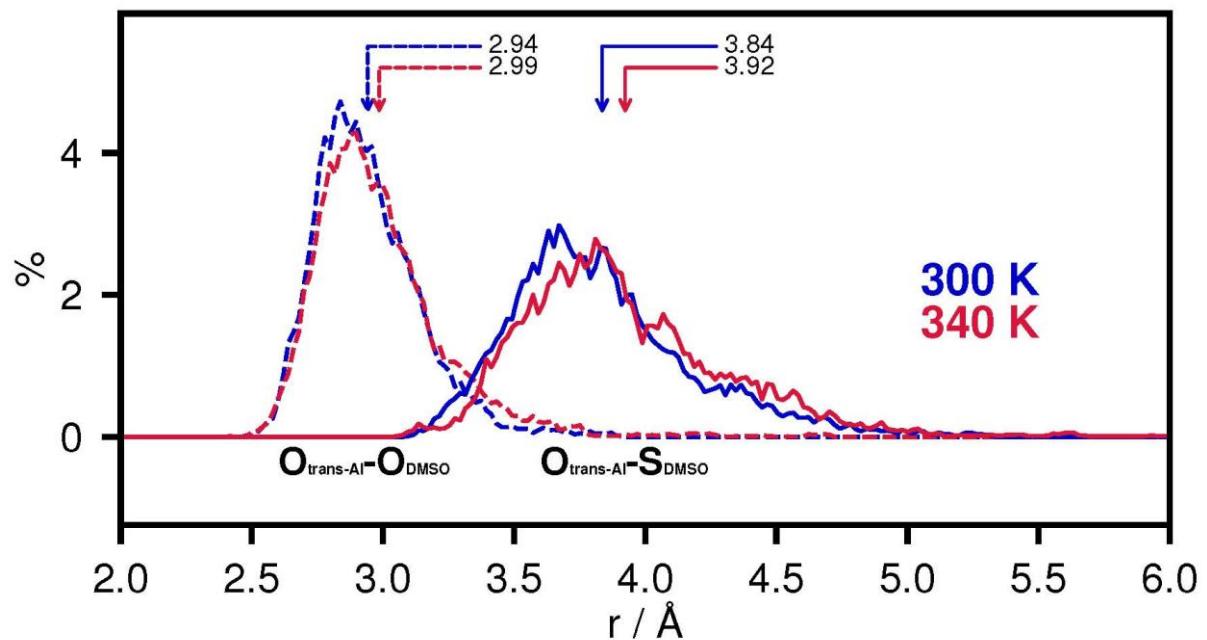


Figure S1: Distribution of distance between the oxygen atom of trans-Al and the oxygen/sulfur atom of DMSO, obtained from the FPMD trajectories at different temperatures (BLYP-D3).

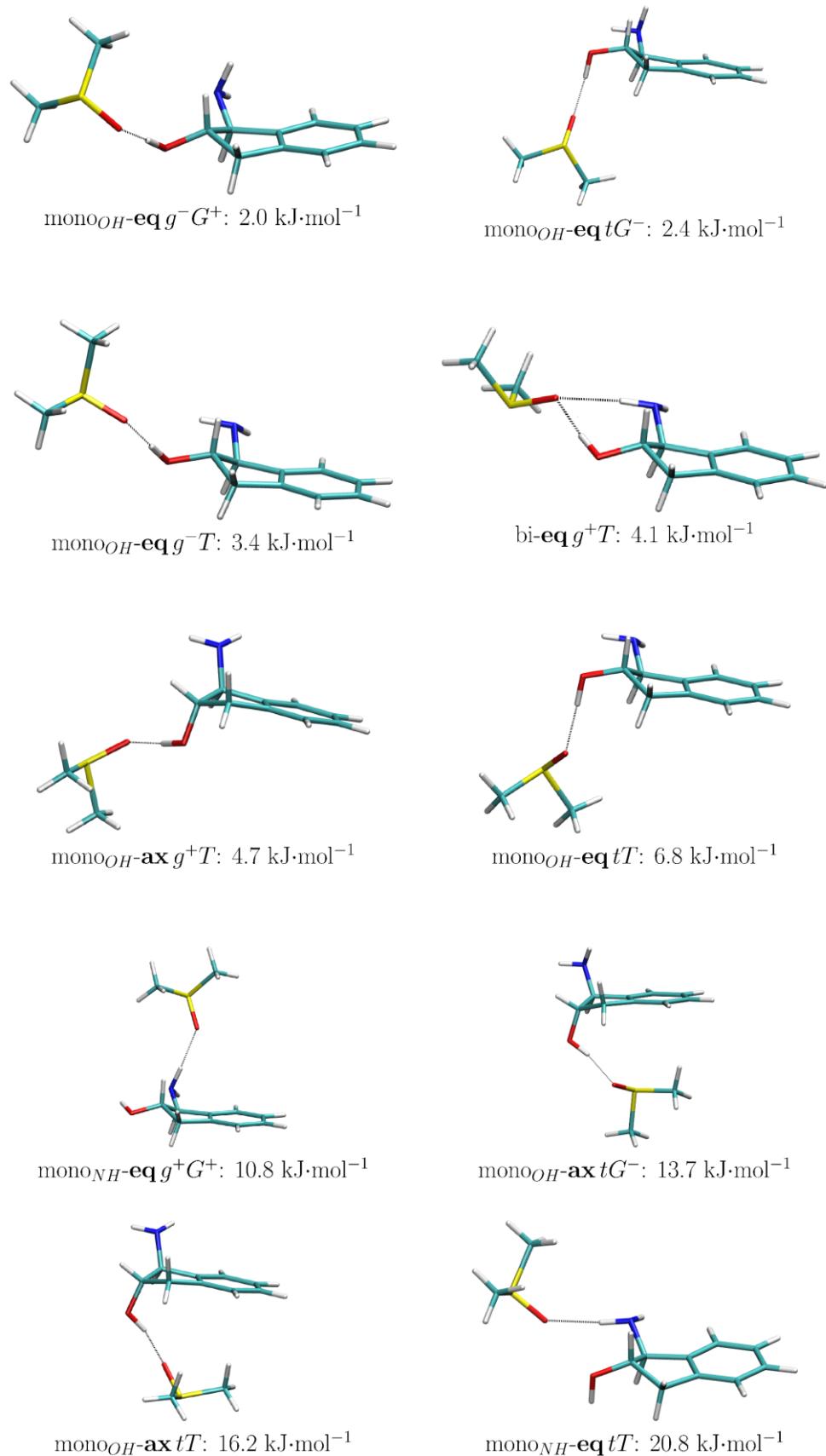


Figure S2: Stable calculated structure of the *trans*-Al:DMSO₆ 1:1 complex at the B3LYP/6-311G++(d,p) level in a DMSO continuum.

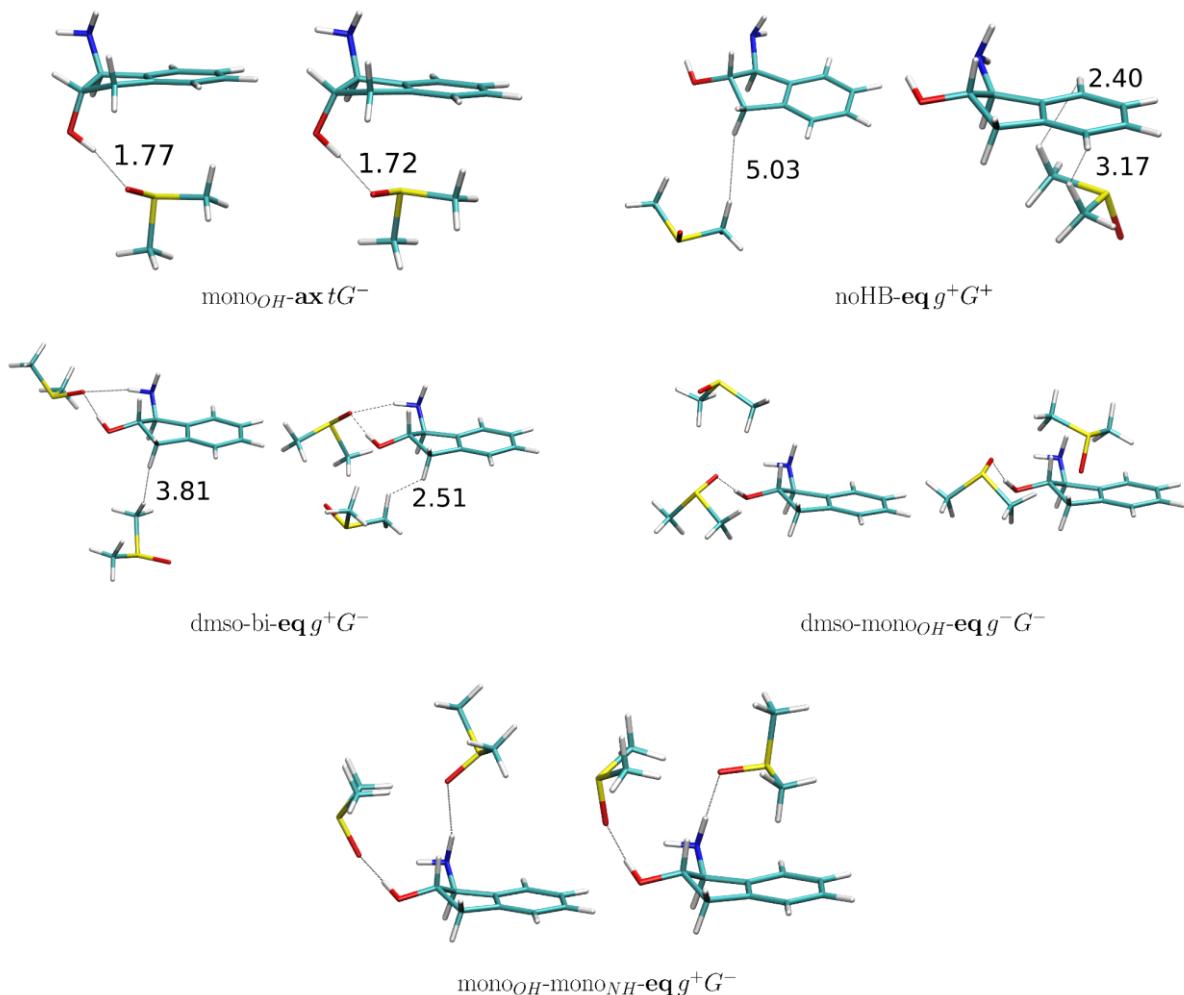


Figure S3: Comparison between the geometry calculated at the B3LYP/6-311G++(d,p) level without (left) or with (right) dispersion correction for a selection of *trans*-Al:(DMSO₆) 1:1 and *trans*-Al:(DMSO₆)₂ 1:2 complexes.

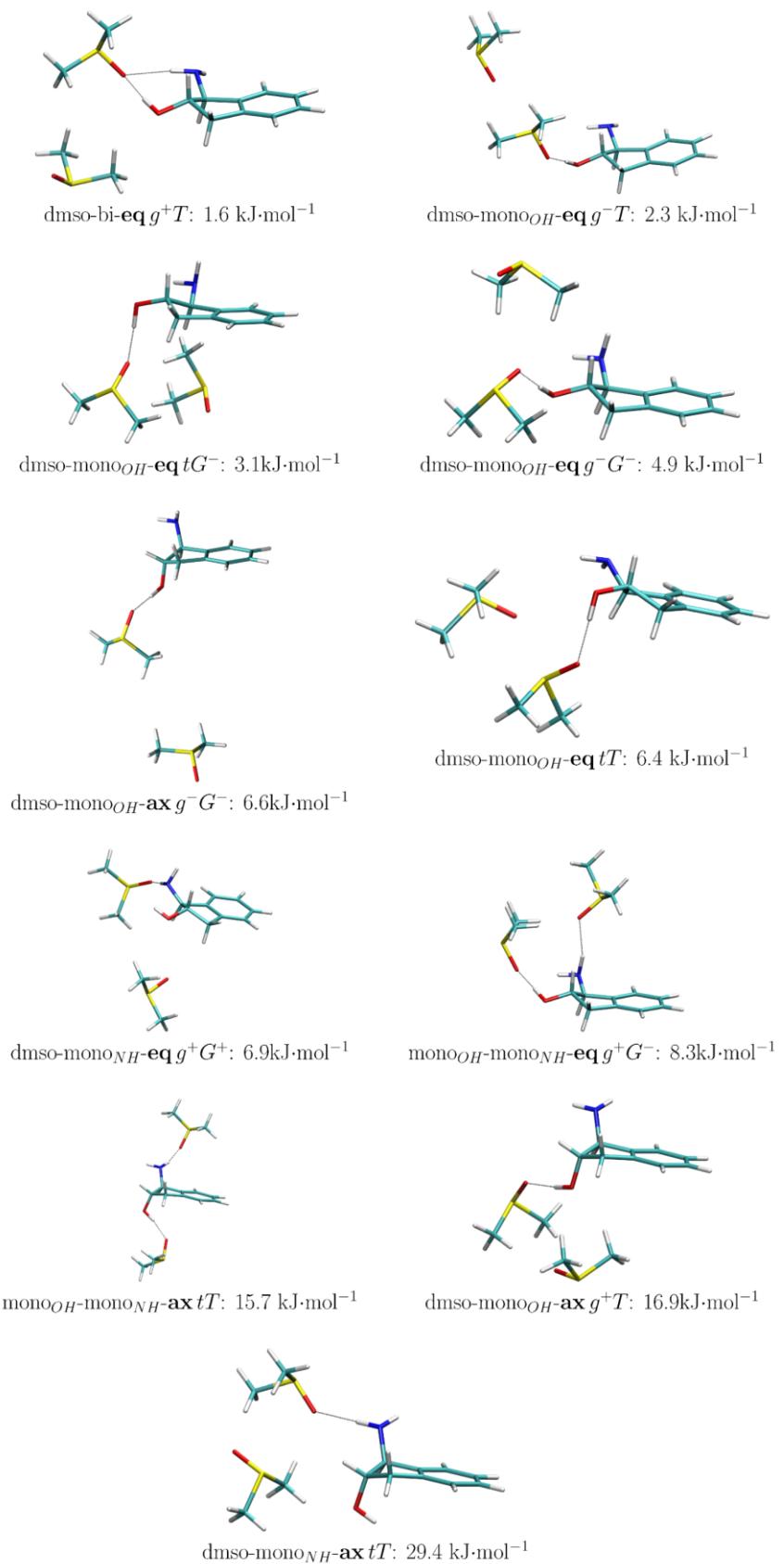


Figure S4: Stable calculated structure of the *trans*-Al:(DMSO)₆ 1:2 complex at the B3LYP/6-311G++(d,p) level in a DMSO continuum.

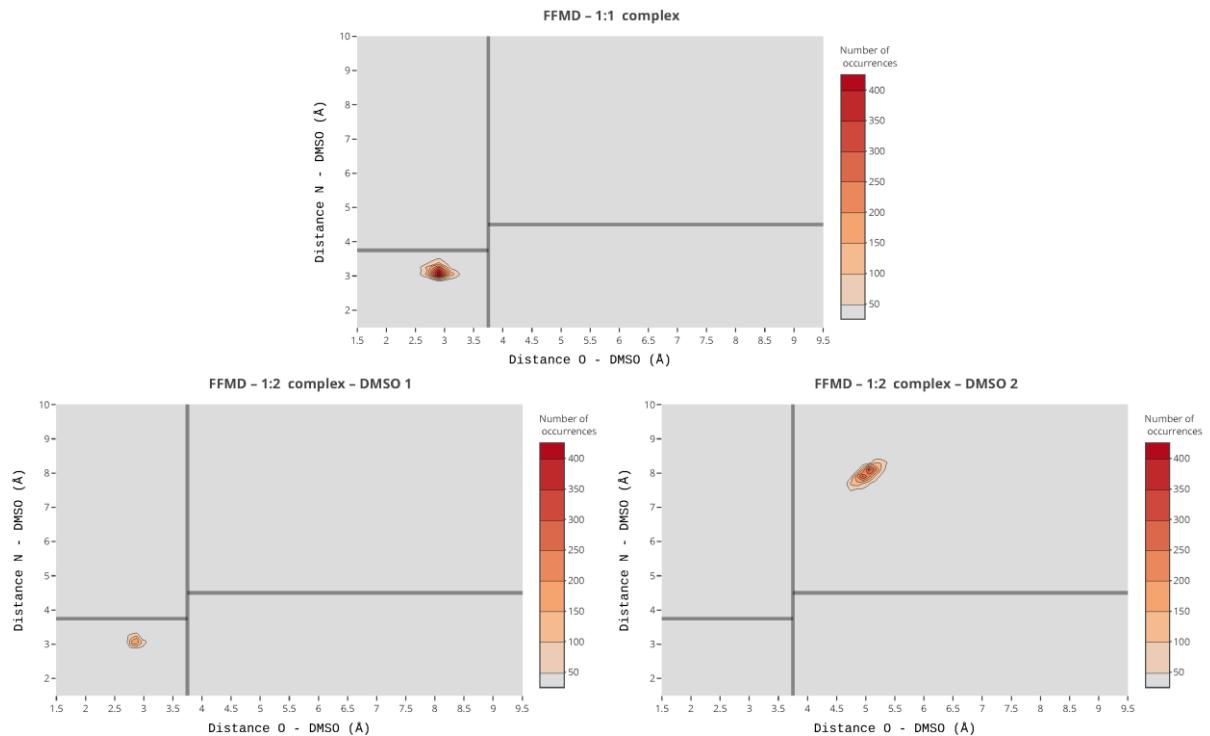


Figure S5: Contour plots of occurrence of O(*trans*-Al)-DMSO and N(*trans*-Al)-DMSO distances in the *trans*-Al:(DMSO_d₆) 1:1 and *trans*-Al:(DMSO_d₆)₂ 1:2 equatorial complexes at 150 K in FFMD simulations.

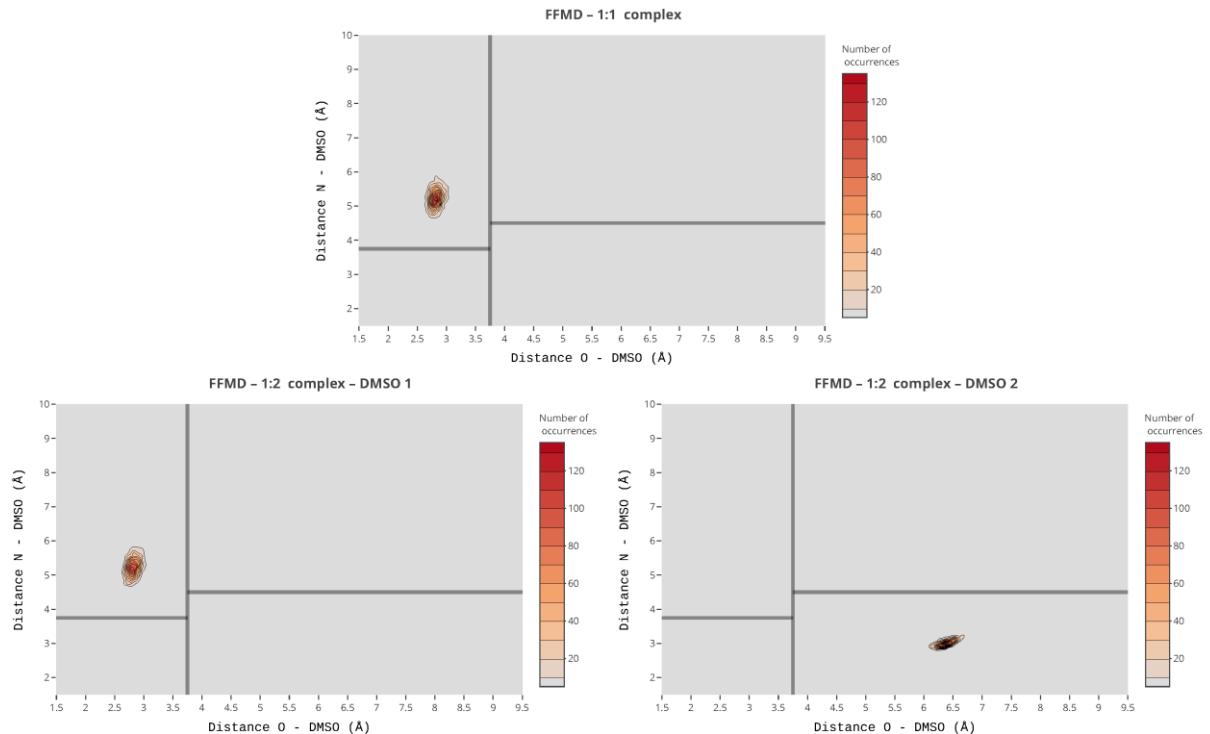


Figure S6: Contour plots of occurrence of O(*trans*-Al)-DMSO and N(*trans*-Al)-DMSO distances in the *trans*-Al:(DMSO_d₆) 1:1 and *trans*-Al:(DMSO_d₆)₂ 1:2 axial complexes at 150 K in FFMD simulations.

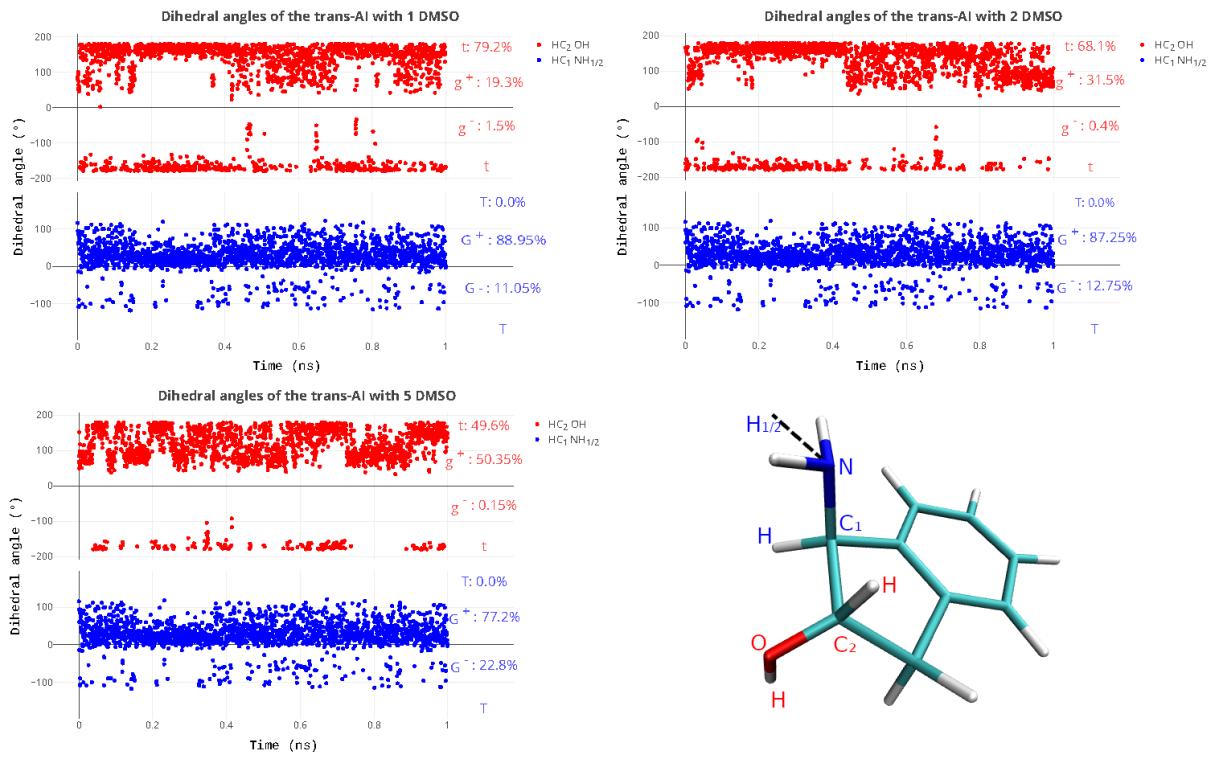


Figure S7: Dihedral angles describing the geometries of the hydroxyl (red) and amino groups (blue) of *trans*-Al during the FFMD simulations at 300 K with one, two and five DMSO.

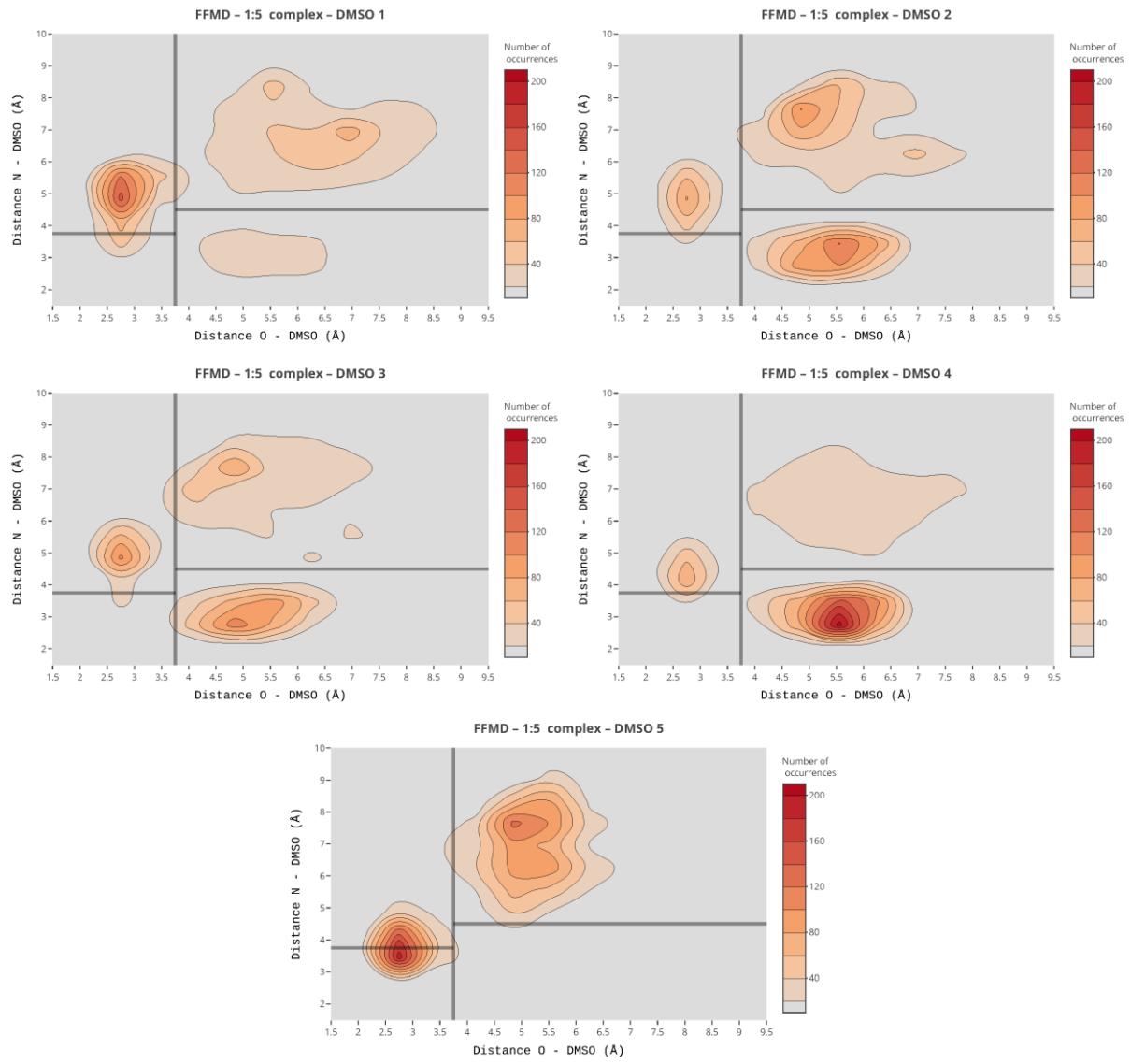


Figure S8: Contour plots of occurrence of O(*trans*-Al)-DMSO and N(*trans*-Al)-DMSO distances for the five DMSO molecules in the *trans*-Al:((DMSO)₆)₅ complex during the FFMD simulations at 300 K.

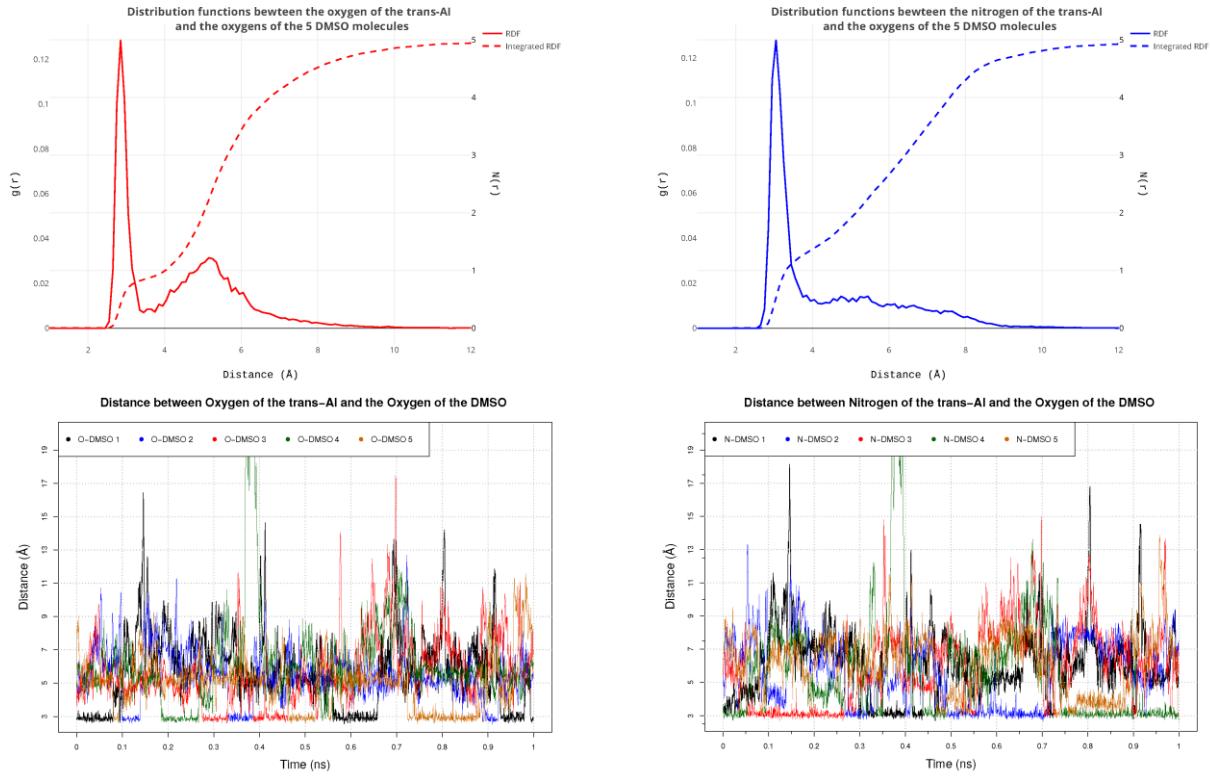


Figure S9: Radial distribution functions (RDF) (top) and distance evolution (bottom) as a function of time for the *trans*-Al:(DMSO₆)₅ 1:5 complex at 300 K, left: O(*trans*-Al)-O(DMSO), right: N(*trans*-Al)-O(DMSO).

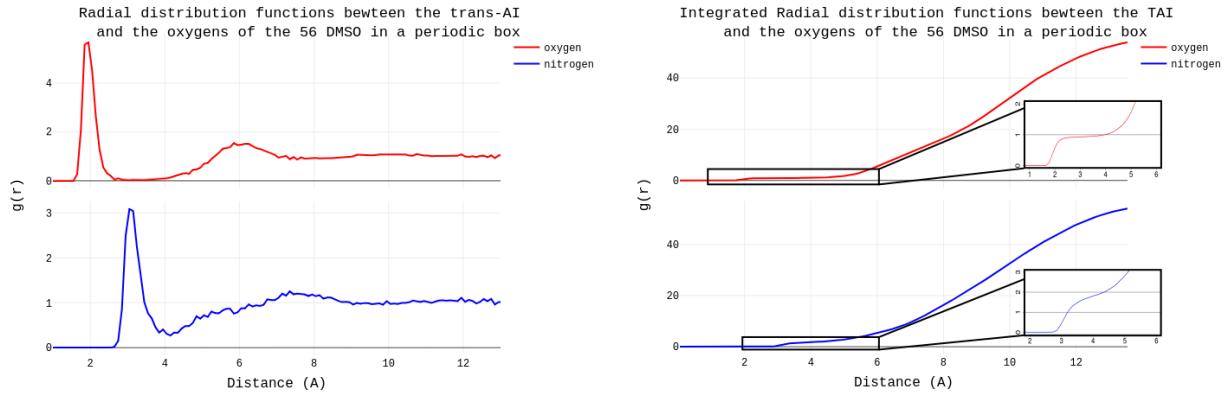


Figure S10: Radial distribution functions (RDF) for *trans*-Al in a box of 56 DMSO molecules at 300 K. The RDF between the oxygen of the *trans*-Al and the DMSO molecules (red) shows an intense peak at 2 Å while the RDF between the nitrogen and the DMSO molecules (blue) shows an intense peak at 3 Å.

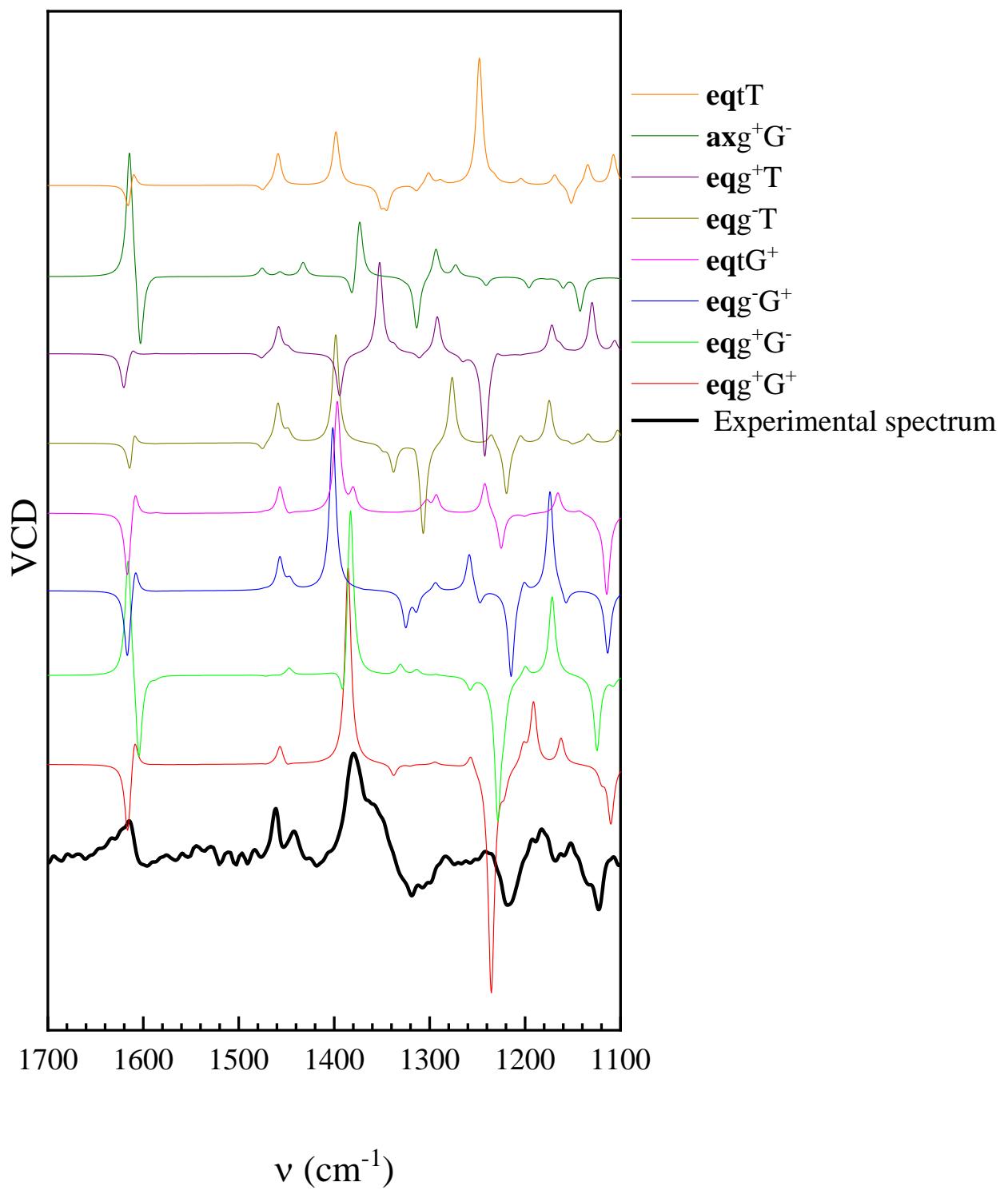


Figure S11: Simulated VCD spectra of the most stable conformers of *(S,S)-trans*-Al.

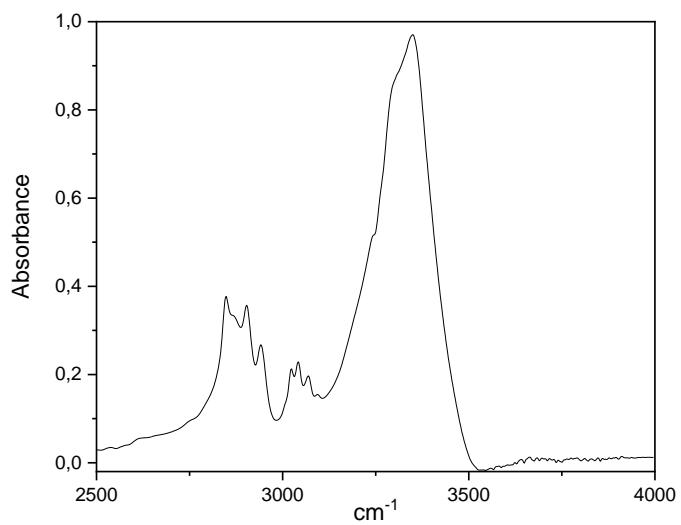


Figure S12: Absorption spectrum of *trans*-Al in a DMSO solution, in the 3 μm region.

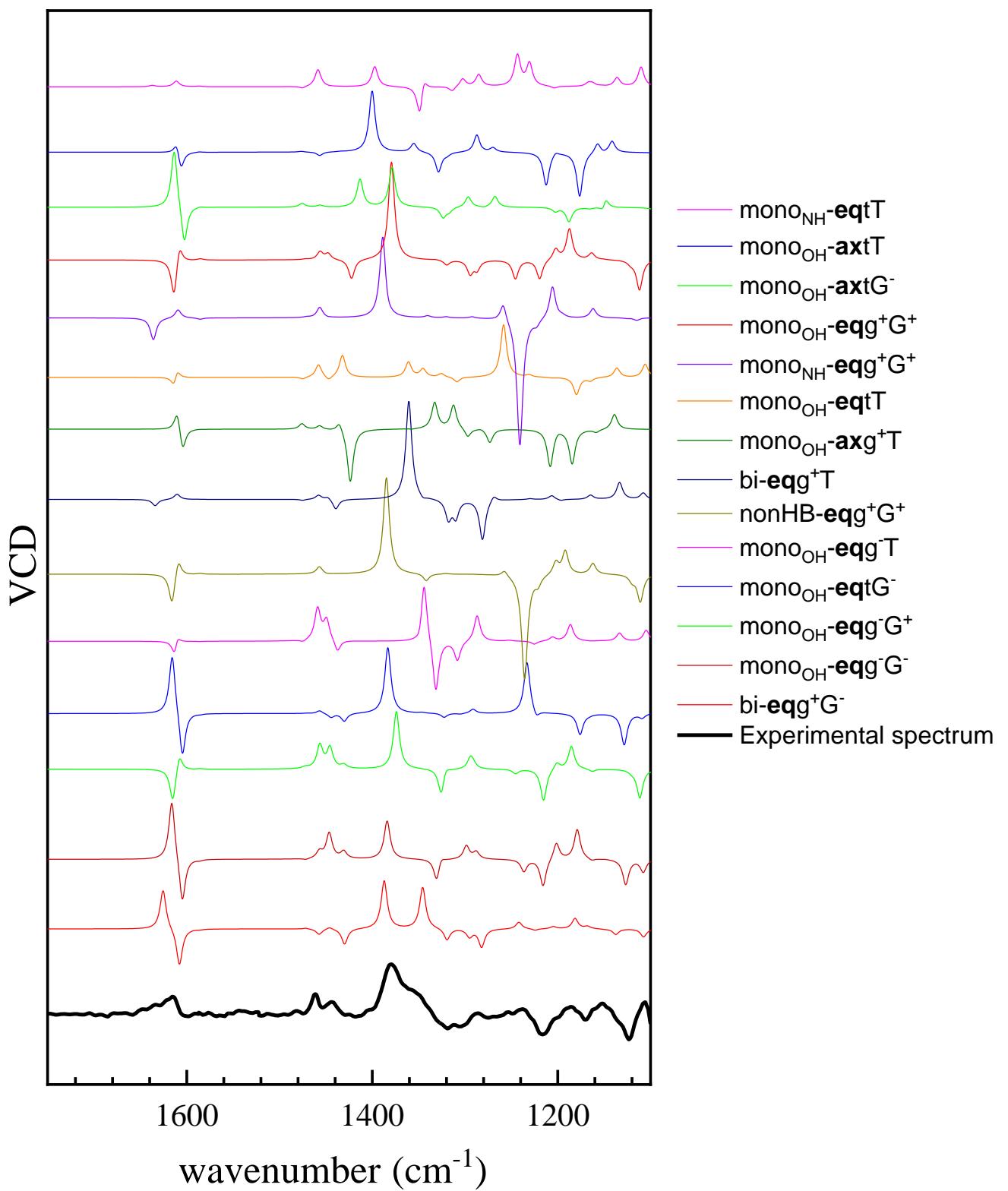


Figure S13: Simulated VCD spectra of the most stable conformers of the *(S,S)-trans*-AI:(DMSO_d₆) 1:1 complexes in a DMSO continuum calculated at the B3LYP/6-311++G(d,p) level.

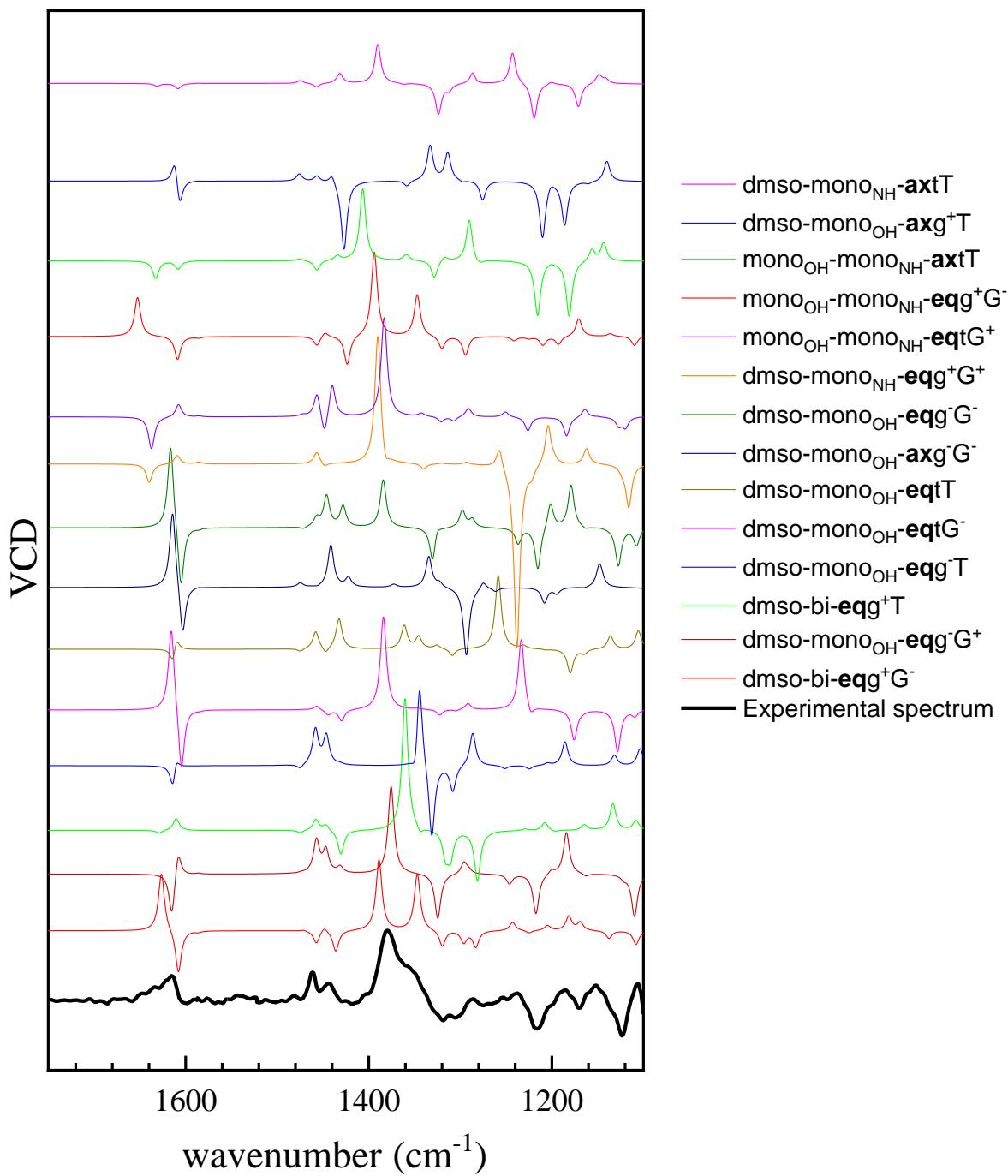


Figure S14: Simulated VCD spectra of the most stable conformers of the *(S,S)**trans*-Al:(DMSO d_6)₂ 1:2 complexes in a DMSO continuum calculated at the B3LYP/6-311++G(d,p) level.

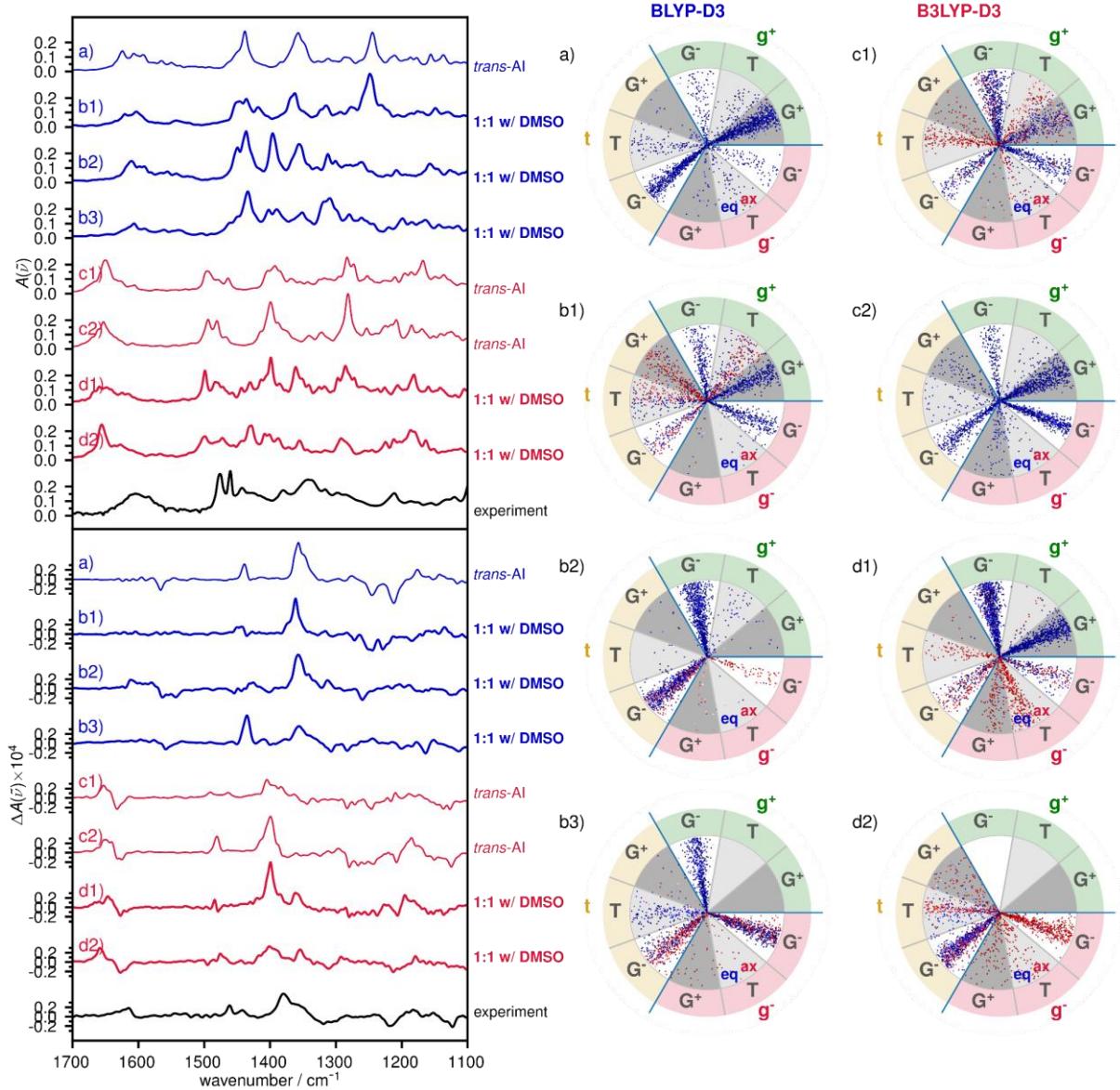


Figure S15: Left: IR and VCD spectra obtained for individual FPMD BLYP trajectories (blue colour) for the monomer (a) and the 1:1 complex (b₁ to b₃), together with sampling clocks (right). Same for B3LYP trajectories (red colour) for the monomer (c₁ to c₂) and the 1:1 complex (d₁ to d₂). Sampling clock (right), displaying how the conformational space of (S,S)-trans-AI is visited by the FPMD trajectory. The circle is divided in regions of OH orientation and sub-divided in regions of NH₂ orientation, using the notation of the static cluster analysis. The density of points is therefore proportional to the abundance of the corresponding conformation, whereas points in blue and red indicate equatorial and axial conformations, respectively.

