Supporting Information

Low-frequency Raman Optical Activity Provides Insight into Structure of Chiral Liquids

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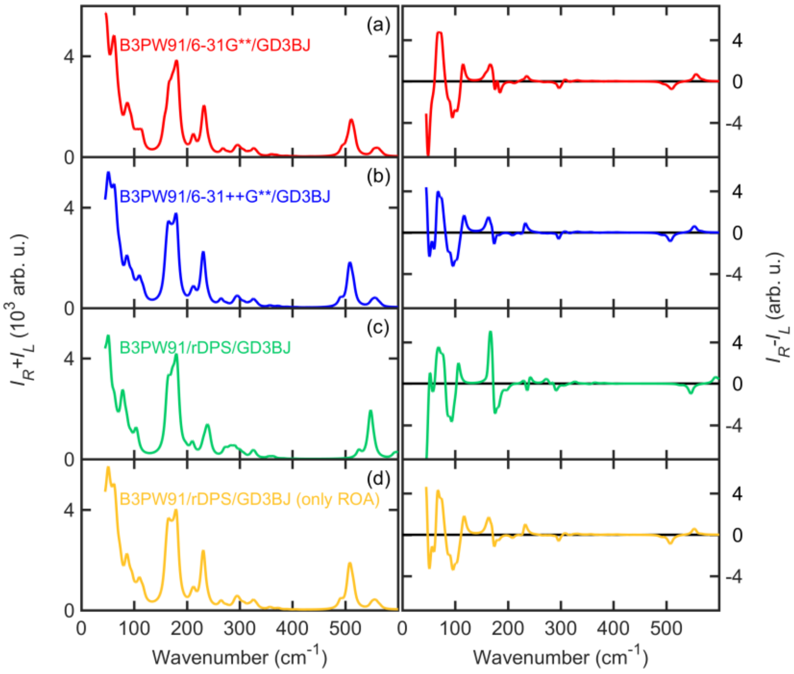

Figure S1. Raman and ROA spectra simulated for one snapshot of nitrile and three basis sets. For rDPS (d) the frequencies were calculated at the B3PW91/6-31++G**/COSMO(ACN)/GD3BJ level.

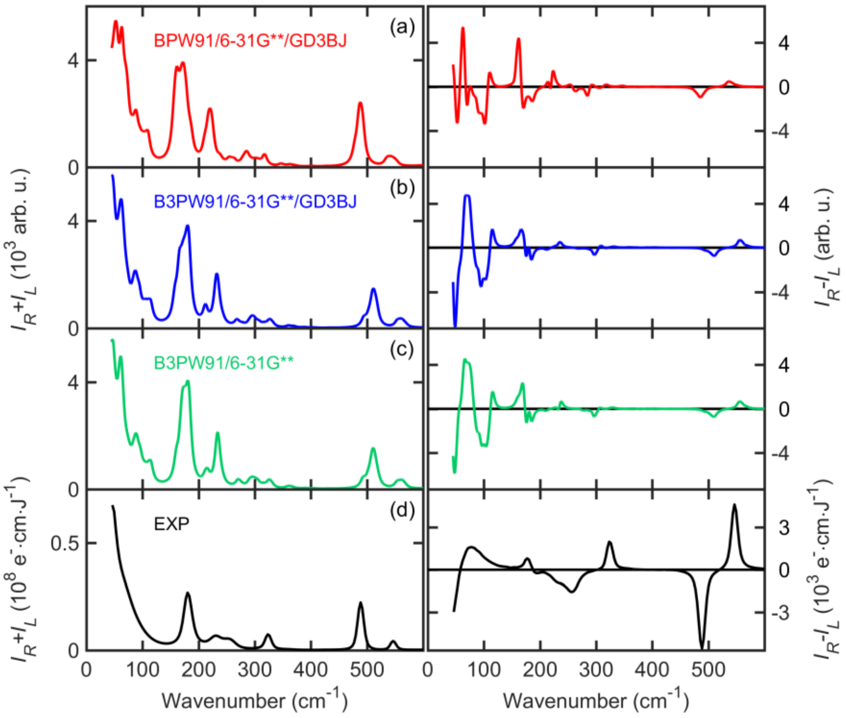

Figure S2. Nitrile Raman and ROA spectra calculated with the B3PW91 and BPW91 functionals, for B3PW91 with and without the GD3BJ dispersion correction, for the 6-31G** basis set and COSMO(ACN) solvent model.

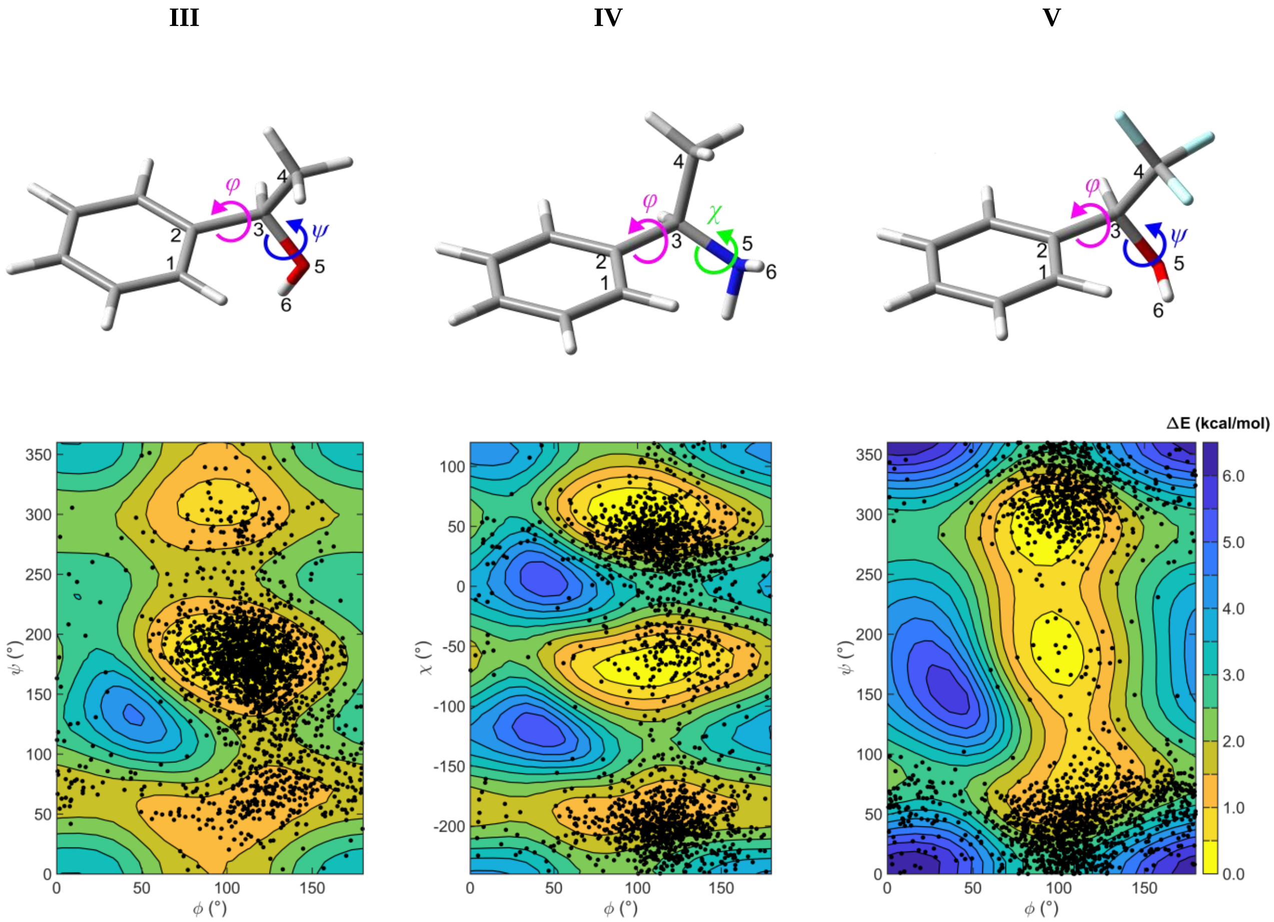

Figure S3. Dependencies of the electronic energy on selected torsion angles calculated at the B3PW91/6-311++G**/COSMO(benzylalcohol) level (contour map) and coordinates from 200 MD snapshots (black dots). The describe phenyl rotation, φ = C1-C2-C3-C4, hydroxyl rotation, ψ = C4-C3-O5-H6, and amine rotation, χ = C2-C3-N5-H6.

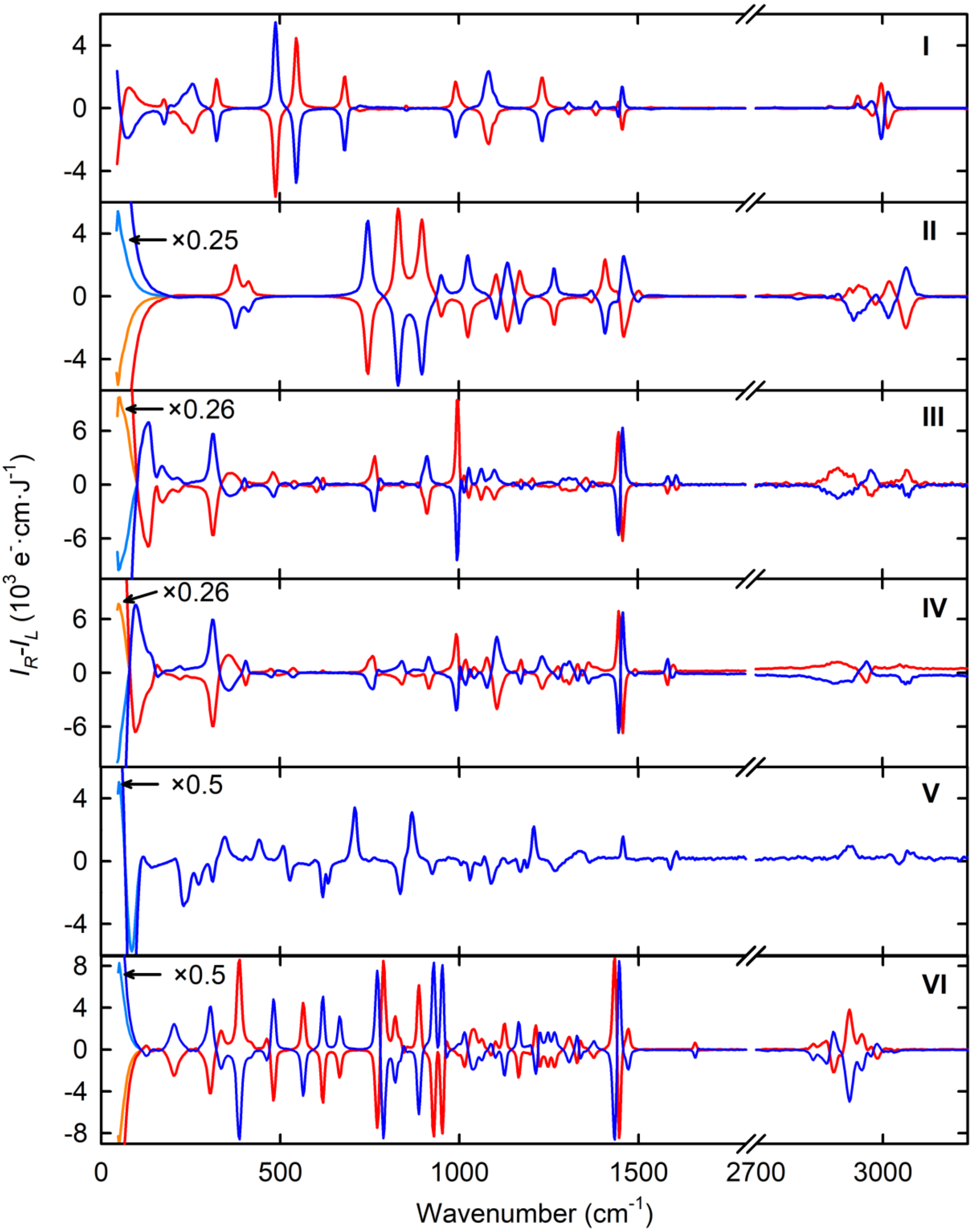

Figure S4. Experimental ROA spectra of the neat liquids, **I** 2-chloropropionitrile, **II** methyloxirane, **III** 1-phenylethanol, **IV** α-methylbenzylamine, **V** α-(trifluoromethyl)benzyl alcohol, and **VI** α-pinene. *R* and *S*-enantiomers are marked in red and blue, respectively.

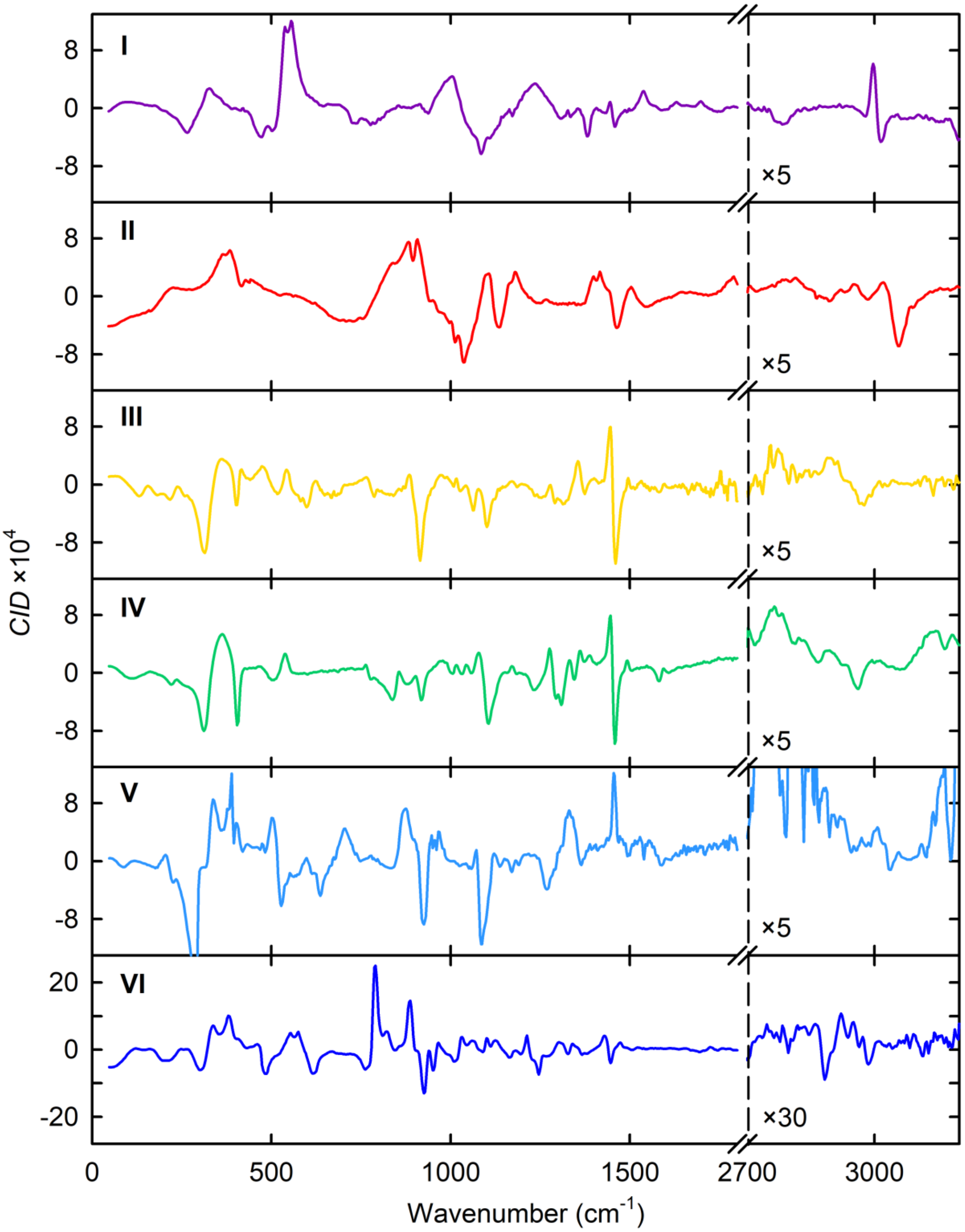

Figure S5. Experimental CID (ROA/Raman) ratios of **I** (*R*)-2-chloropropionitrile, **II** (*R*)-(+)-propylene oxide, **III** (*R*)-(+)-1-phenylethanol, **IV** (*R*)-(+)-α-methylbenzylamine, **V** (*S*)-(+)-α-(trifluoromethyl)benzyl alcohol, and **VI** (+)(1R,5R)-α-pinene.

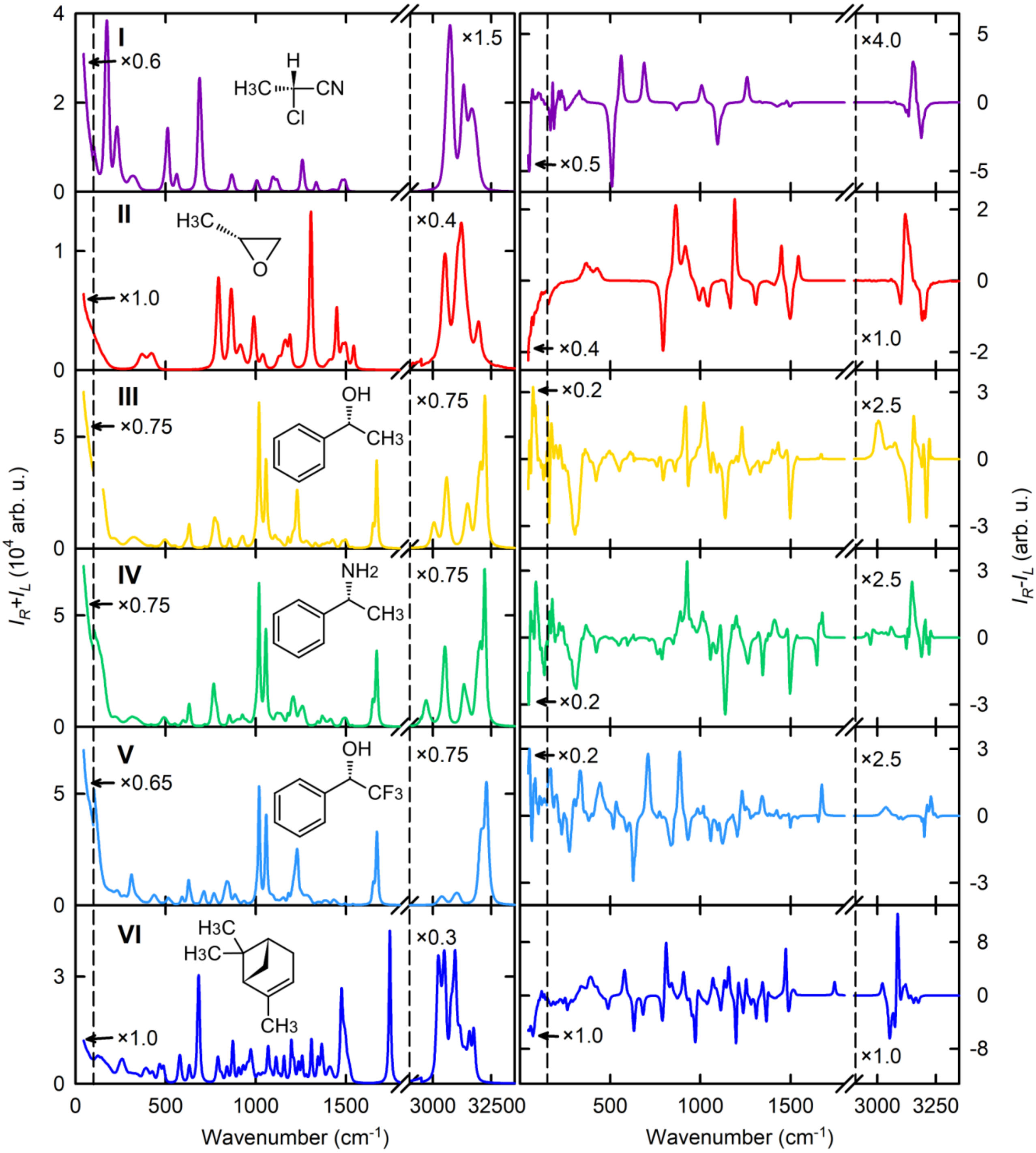

Figure S6. Raman and ROA spectra of **I**-**VI** simulated in the whole range, the crystal model.

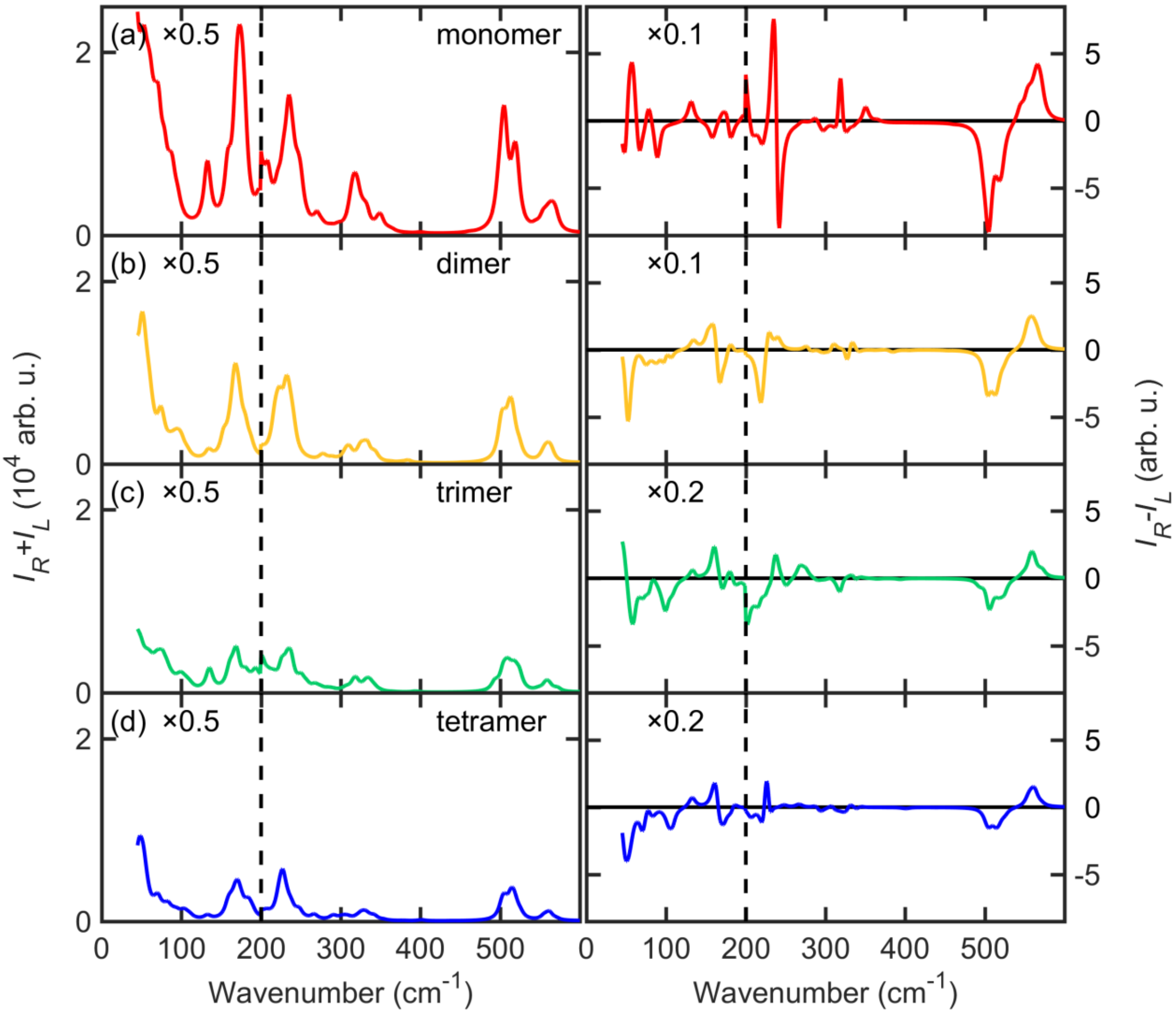

Figure S7. Raman and ROA spectra of one nitrile MD snapshot (10 molecules in the elementary cell) simulated from force field constructed from monomers, dimers, trimers and tetramers.

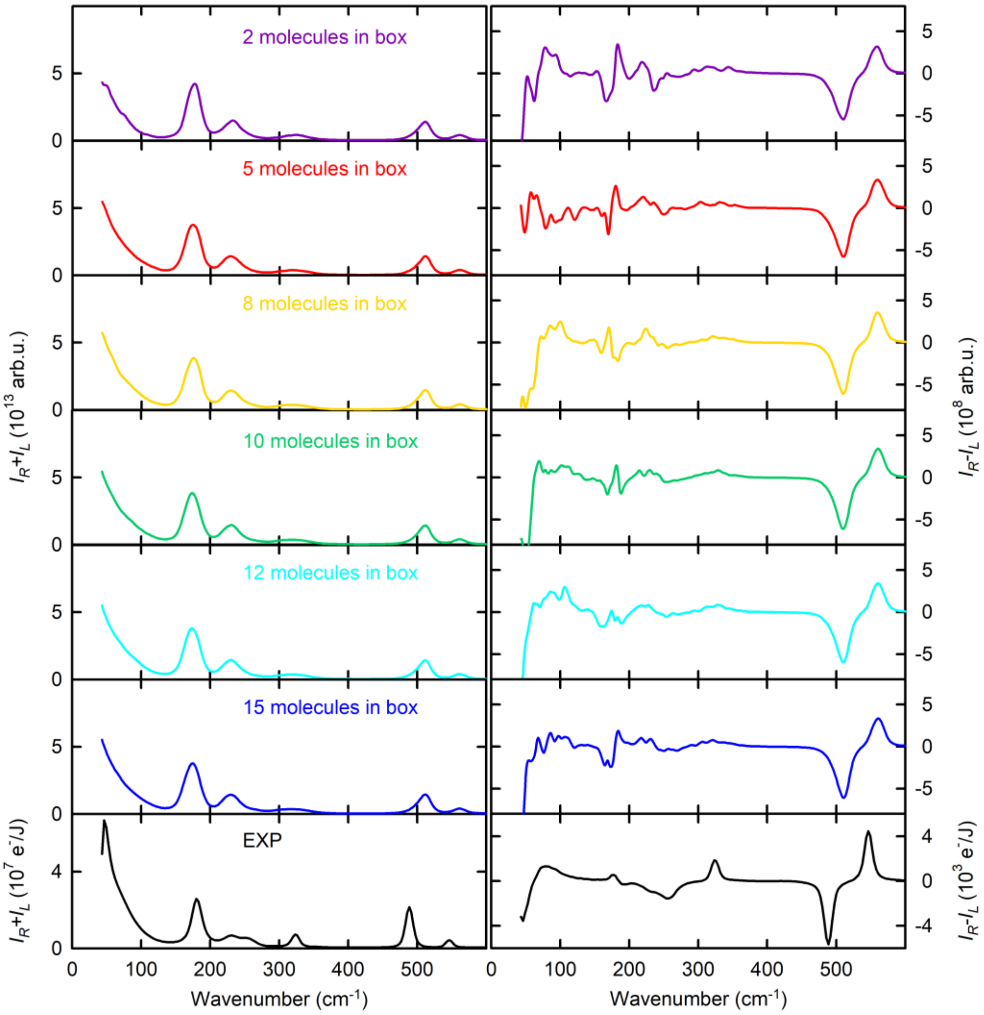

Figure S8. Calculated Raman and ROA nitrile spectra, using elementary cells containing 2, 5, 8, 10, 12 and 15 molecules, for 200 snapshots.

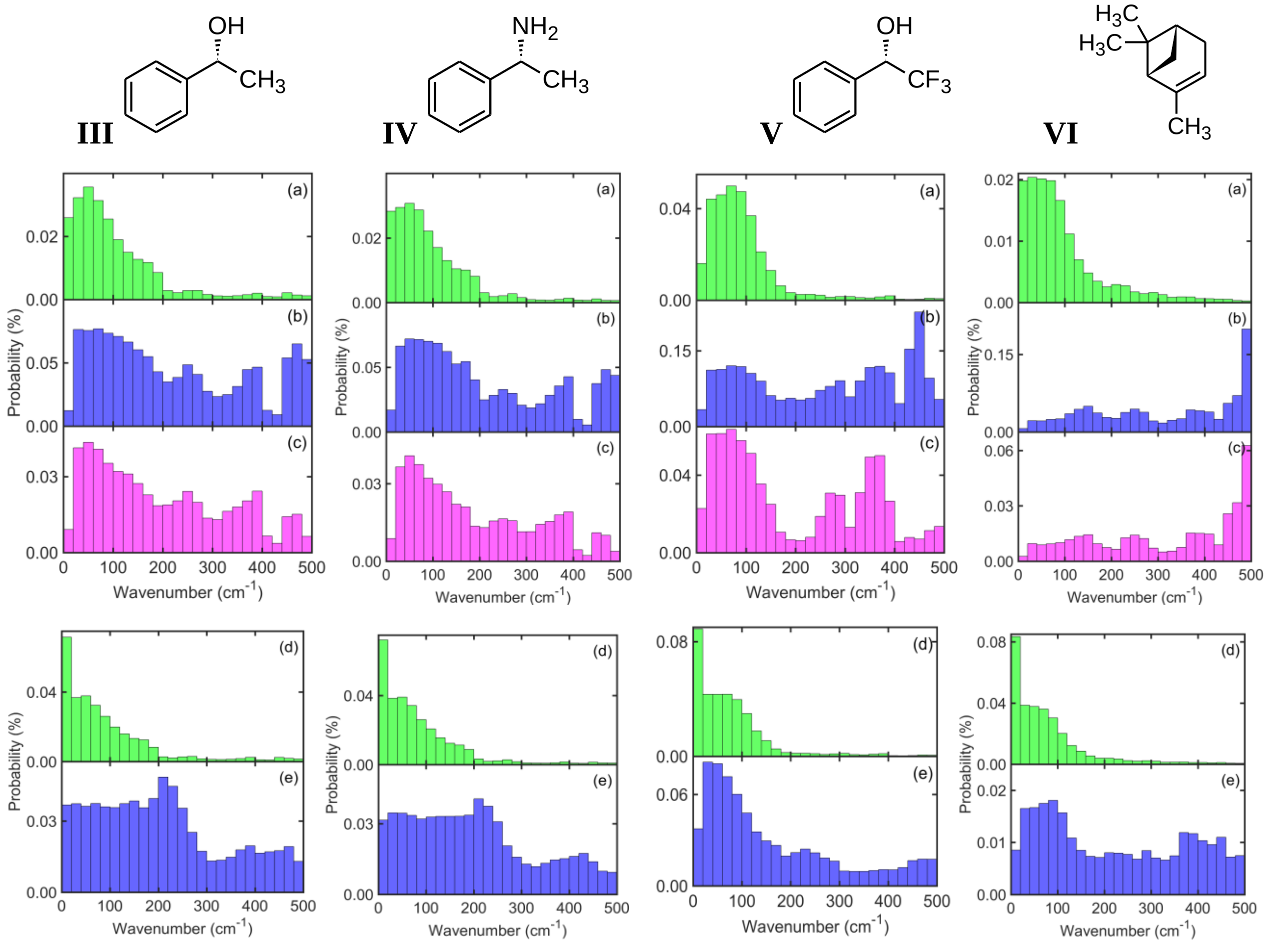

Figure S9. Relative vibrational potential energy distribution (PED) of intermolecular motions related to two (stretching (a), bending (b), torsion (c)) and one (translations (d), rotations (e)) molecule, for **III-V**.

PEDs of individual coordinates were calculated by the following procedure.

1) Transformation matrix **B** was defined, relating internal (I_i) and Cartesian (r_λ) coordinates, $I_i = \sum_\lambda B_{\lambda i} r_\lambda$. Using **B**, force field elements f_{ij} in the internal coordinates were calculated.

2) Within the harmonic approximation, Cartesian force field was normalized, so that the **S** matrix relating Cartesian and normal mode (Q_J) coordinates was obtained, $Q_J = \sum_\lambda S_{\lambda J} r_\lambda$

3) Relative energy contribution of coordinate I_i in mode J was calculated as $PED_{Ji} = \frac{A_{Ji}}{\sum_i A_{Ji}} \times 100\%$, where $A_{Ji} = b_{Ji}^2 f_{ii} \omega_J^{-1}$, $b_{Ji} = \sum_\lambda S_{\lambda J} B_{\lambda i} \sqrt{m_\lambda}$, ω_J is the normal mode frequency, m_λ is atomic mass. In the graphs, PED values were averaged over the snapshots and normal modes in a wavenumber interval.

Table S1 Laser powers at the sample *P* and total accumulation times *t* used in ROA measurements.

Compound	Enantiomer	*P* (mW)	*t* (h)
I nitrile	*R*	83	9.7
	S	83	13.2
II methyloxirane	*R*	540	34.6
	R @ water	338	5.5
	S	540	19.3
III phenylethanol	*R*	86	1.9
	S	82	2.9
IV benzylamine	*R*	69	7.8
	S	69	8.5
V 3F-benzyl	*S*	114	11.4
	R	266	5.5
VI α-pinene	*S*	266	5.5

Table S2. Dimensions of the elementary cells (10 molecules in the box) and densities used in the calculations

	Liquid	Box size (Å)	ρ (g/ml)	COSMO Solvent
I	nitrile	11.37	1.012	acetonitrile
II	methyloxirane	10.39	0.859	tetrahydrofuran
III	phenylethanol	12.61	1.012	benzylalcohol
IV	benzylamine	12.89	0.940	benzylalcohol
V	3F-benzyl	13.13	1.293	benzylalcohol
VI	α-pinene	13.82	0.858	cyclohexane

Table S3. Selected low-frequency fundamental modes in **III**-**V**.

v / cm-1	**modes**
III:	
36	Phe rotation
128	Me and Phe wagging
212	Me and Phe scissoring
266	Me and OH rotation
283	Me and OH rotation
305	deloc. def.
372	deloc. def.
411	Phe out of plane
482	deloc. def.
IV:	
29	Phe rotation
129	Me and Phe wagging
214	Me and Phe scissoring
268	Me rotation
303	deloc. def., NH_2 rotation
360	deloc. def.
411	Phe out of plane
480	NH_2 and Me wagging
V:	
27	Phe rotation
64	CF_3 rotation, Phe wagging
99	deloc. def.
199	OH rotation
233	deloc. def.
290	deloc. def.
308	deloc. def.
335	deloc. def.
412	Phe out of plane
428	deloc. def.