Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Principal Component Analysis to Enhance Enantioselective Raman Spectroscopy

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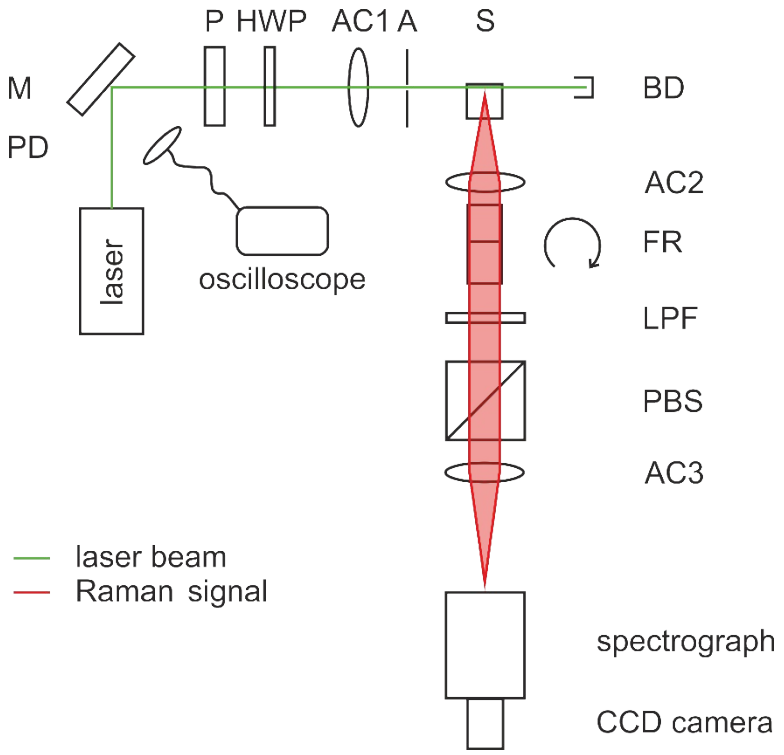

Fig. S1: Schematic of 90° enantioselective Raman set-up. A: aperture, AC: achromatic lens, BD: beam dump, FR: half-wave Fresnel rhomb, HWP: half-wave plate, LPF: longpass filter, M: mirror, P: polarizer, PD: photo diode, S: sample.

Tab. S1 Peak assignment for Raman and ATR-FTIR spectra of 4-methylpentan-2-ol: str.=stretching, def.=deformation, sciss.=scissoring, rock.=rocking, wagg.=wagging, tors.=torsion, s=symmetric, as=antisymmetric, sh=shoulder, FR=Fermi resonance.

Raman wavenumber /cm^{-1}	**FTIR wavenumber /cm^{-1}**	**own assignment**	**Reference**
338		CCC def.	[1]
353(sh)		CCO def., CCC def.	[1]
386		CCC def.	[1]
428		CCO def., CCC def.	[1]
442		CCO def., CCC def.	[1]
462		CCO def., CCC def.	[1]
489		CCO def., CCC def	[1]
518		CCO def., CCC def.	[1]
780		CH_2 rock.	[1]
818 (sh)		CC str.	[1]
826	826	$(C)_2CO$ s str.	[2]
844 (sh)	846 (sh)	CH_2 rock., CH_3 rock.	[1]
878	880	CC str.	[1]

921	924	CC str., CH_3 rock.	[1]
951		CC str., CH_3 rock., CO str.	[1]
963		CC str., CH_3 rock., CO str.	[1]
	972	CO str., CC str.	[1]
1012	1017	CO str., CH_2 tors.	[1]
1039 (sh)		CO str., CH_2 tors.	[1]
1049		CC str.	[1]
	1056	CO str., CC str.	[1]
1107 (sh)		CH_3 rock.	[1]
	1115	CH_2 rock.	[1]
1126 (sh)		CH_2 rock. $(C)_2CO$ as str.	[1] [2]
1142	1140 (sh)	$(C)_2CO$ as str.	[2]
1157 (sh)	1154	$(C)_2CO$ as str.	[2]
	1169	$(C)_2CO$ as str.	[2]
1224		CH_2 rock., CH_3 rock.	[1]
	1234	CH_2 rock., CH_3 rock.	[1]
	1275	CH_2 wagg., COH def.	[1]
1308 (sh)	1312	COH def.	[1]
1325		CH_3 s def.	[3]
	1332	CH_3 s def.	[3]
	1345	CH_3 s def.	[3]
	1370	CH_3 s sciss. $CH(CH_3)_2$ sciss.	[2] [2]
	1383 (sh)	$CH(CH_3)_2$ sciss.	[2]
	1413	CH_2 sciss.	[1]
	1425 (sh)	CH_2 sciss.	[1]
1433		CH_2 sciss.	
1441		CH_3 as def. CH_3 as sciss.	[3] [2]
	1459 (sh)	CH_3 as sciss.	[2]
	1469	CH_3 as def.	[1]
2713		Combination	[1]
	2724	Combination	[1]
2756		Combination	[1]
	2841 (sh)	Overtone	[1]
2875	2874	CH_2 s str	[1, 2]
2894		CH_2 s str., FR	[2]
2908 (sh)		CH_2 s str.	[1]
	2920	CH_2 FR	[2]
2931	2931 (sh)	CH_3 s str	[1]
2964	2960	CH_2 as str.	[1]
3360	3344	OH str.	[1]

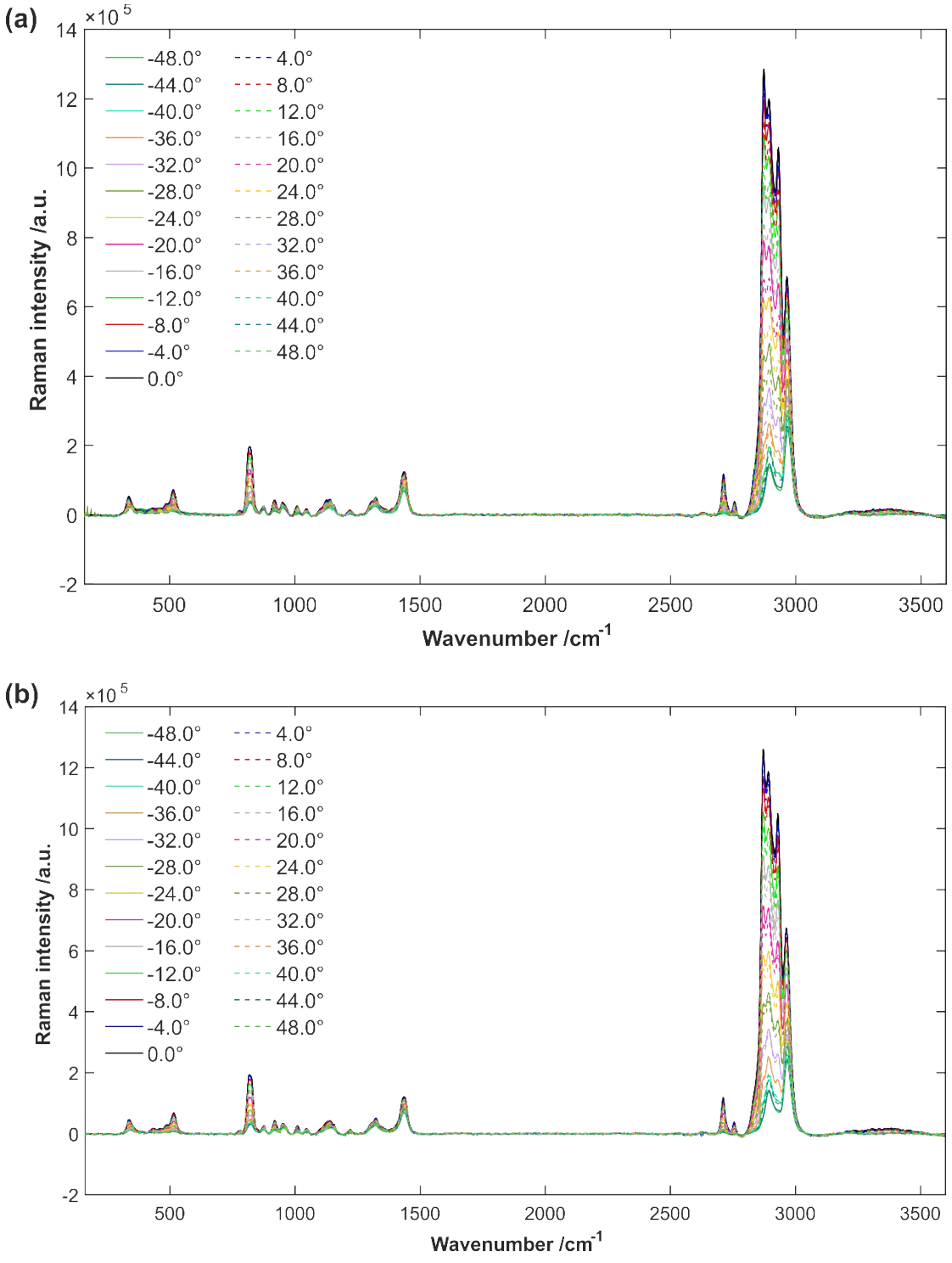

Fig. S2 Retarder-resolved Raman spectra of (2R)-(–)-4-methylpentan-2-ol (a) and (2R2S)-(±)-4-methylpentan-2-ol in the range –48.0° ≤ θ ≤ 48.0° in steps of 4.0°.

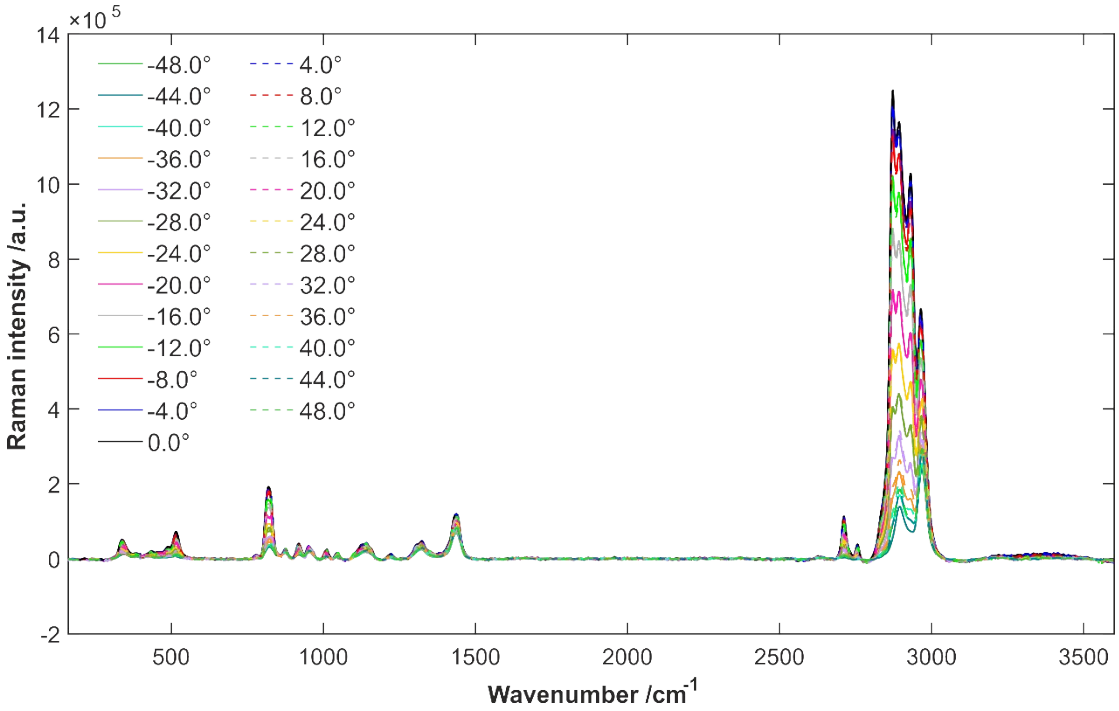

Fig. S3 Retarder-resolved Raman spectra of (2S)-(+)-4-methylpentan-2-ol in the range –48.0° ≤ θ ≤ 48.0° in steps of 4.0°.

The parameters in Tab. S2 are obtained using the esR spectra of (2*R*2*S*)-(±)-4-methylpentan-2-ol in Fig. S2 (b). The relative Raman intensities $^{\Delta I^{B}_{rel}}$ of a medium B are calculated according to eq. (S1)-(S3) with one simplification. The depolarization ratio of a vibrational band is assumed to be equal for all three media, i.e. is independent of the optical rotation α. For a more accurate analysis, the depolarization ratio has to be calculated dependent on α.[4]

Tab. S2 Parameters for calculation of relative Raman intensity differences according to eq. (S1)-(S3).

Wavenumber /cm^{-1}	Depolarization ratio	Amplitude A	Minimum Intensity I_{min}	b_{rac} /°	$b_{(-)}$ /°	$b_{(+)}$ /°
2894	0.24	0.880	0.120	0.0	1.5	-1.5
2964	0.73	0.362	0.208	0.0	1.5	-1.5

The retarder-resolved intensity for a vibrational band (vib) at the angle of the half-wave retarder θ_i can be calculated according to eq. (S1) with the Amplitude A_{vib}, the minimum intensity $I_{\text{min,vib}}$ and the shift b of the maximum intensity along θ (b=¬α).

$$I_{vib}(\theta_i) = A_{vib}\, cos^2(2\theta_i + b) + I_{min,\,vib} \tag{S1}$$

Normalizing the intensity of a vibrational band (vib1) with respect to the corresponding intensity of a vibrational band (vib2) with different symmetry delivers

$$I_{norm,vib2}^{B}(\theta_i) = I_{vib1}^{B}(\theta_i)/I_{vib2}^{B}(\theta_i) \tag{S2}$$

In a last step, the difference of the normalized intensity and a reference medium $I_{norm,vib2}^{ref}(\theta_i)$, e.g. the racemate, is calculated relatively to the reference medium

$$\Delta I_{rel}^{B}(\theta_i) = \frac{I_{norm,vib2}^{B}(\theta_i) - I_{norm,vib2}^{ref}(\theta_i)}{I_{norm,vib2}^{ref}(\theta_i)} \tag{S3}$$

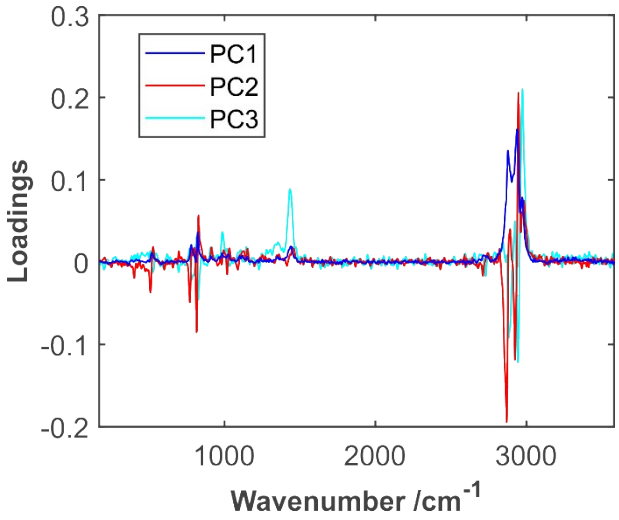

Fig. S4 Loadings of the first three components of the difference Raman spectra of the pure enantiomers of butan-2-ol. PCA conducted with spectra taken from the half-wave retarder angular range -46° $\leq \theta \leq$ ***46°.***

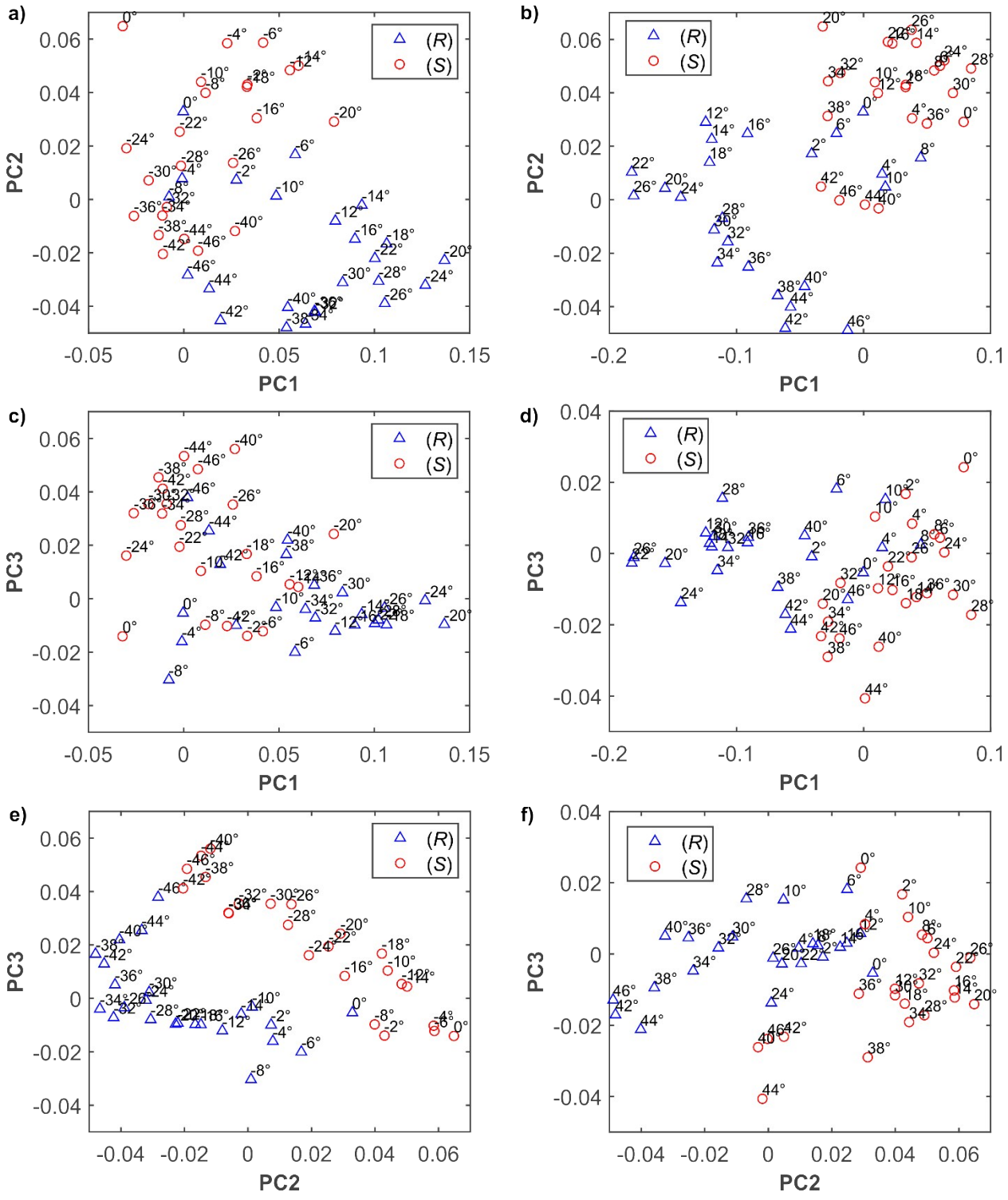

Fig.S5 Principal component analysis (scores) of difference spectra of the pure enantiomers of butan-2-ol with the explained variances of 57.2%, (PC1), 12.4% (PC2), and 5.2% (PC3). For clarity, the results of the analysis are split up into two angular ranges: $-46° \leq \theta \leq 0°$ ***in the left panel (a), c), e)) and*** $0° \leq \theta \leq 46°$ ***in the right panel (b), d), f)). EsR spectra are taken from previous measurements according to Ref.[5].***

References

1. J. Kiefer, S. Wagenfeld and D. Kerlé, *Spectrochim. Acta, Part A*, 2018, **189**, 57-65.
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5. C. C. Rullich and J. Kiefer, *Analyst*, 2018, **143**, 3040-3048.