Supplementary Information for: Terahertz Spectroscopy of Enantiopure and Racemic Polycrystalline Valine

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There are four parts of this Supplementary Information. 1. Unit cell parameters for all instances of valine (without any salts or co-solvents) from the Cambridge Structural Database (CSD).[2] 2. Powder XRD spectra. 3. Plots of the quantified type of motion for the systems studied. 4. Movie files for vibrational modes discussed in the text.

I. Information from the CSD

Sample	Cambridge Database Identifier	Temp (K)	Space Group	Cell Lengths (Å)			Cell Angles (°)		
				a	*b*	*c*	α	β	γ
D-valine	**AHEJEC03[1]**	**293**	**$P2_1$**	**9.673**	**5.252**	**12.043**	**90**	**90.75**	**90**
	AHEJEC02	270	$P2_1$	9.67	5.268	12.026	90	90.72	90
	AHEJEC	223	$P2_1$	9.666	5.257	11.984	90	90.66	90
	AHEJEC01	173	$P2_1$	9.661	5.246	11.941	90	90.59	90
L-valine	**LVALIN[3]**	**295**	**$P2_1$**	**9.710**	**5.270**	**12.060**	**90**	**90.80**	**90**
	LVALIN01	120	$P2_1$	9.682	5.247	11.930	90	90.57	90
	LVALIN02	270	$P2_1$	9.674	5.266	12.020	90	90.72	90
DL-valine	VALIDL02	120	P-1	5.222	5.406	10.838	90.89	92.34	110.02
	VALIDL01	295	-	5.430	11.050	5.250	92.40	109.40	91.00
	VALIDL03[5]	**100**	**P-1**	**5.233**	**5.415**	**10.830**	**90.83**	**92.29**	**110.01**
	VALIDL	295	$P2_1/c$	5.210	22.100	5.410	90	109.20	90

Table S1. The cell parameters of valine found in the CSD.

X-ray powder diffraction measurements are used to confirm the morphology of the samples. Table S1 provides all available entries in the CSD for valine (without any salts or co-solvents). Our samples are found to have the structures shown in bold type. The cell parameters and space groups confirm that the crystals of pure D- and L- enantiomers have the same structure as each other, and the racemate has a completely different crystal structure.

II. Powder XRD Spectra

The atomic coordinates from the CSD are used to calculate x-ray powder patterns using Mercury 1.4.1 software.[4] The experimental and calculated results are then compared to identify the samples based on the main features in the diffraction patterns (see Figure 3 in main text, and Figures S1 and S2). The intensities of the powder patterns are not as important for identification as is the scattering angle, 2θ. Scattering intensities are highly dependent on sample preparation (*e.g.*, anisotropy) and experimental parameters. Pulverizing the samples in a ball mill improves the data considerably by providing more uniform crystallite sizes and eliminating any anisotropies arising from unusual crystal shapes such as needles or plates.[6] Pulverizing the samples for two minutes is sufficient, and longer times causes the peak widths to increase. This could be due the particles becoming so small that their diffraction is broader than the instrument resolution, or because the samples become somewhat amorphous due to heating or mechanical distortion due to thrashing during the pulverization process. The unit cell parameters of the amino acids studied in this work, including any known polymorphs, are presented in Table S1.

Our powder XRD spectra were obtained at room temperature, and unfortunately the only room temperature CSD entry for the triclinic polymorph of DL-valine (VALIDL01) did not include atomic positions, only unit cell parameters. However, by scaling the unit cell dimensions (but not atomic coordinates) of the VALIDL03 structure to match that of VALIDL01, it was possible to identify our sample material as the triclinic form of DL-valine. The calculated diffraction pattern of the approximated room temperature VALIDL03 structure is in good agreement with our data, while the calculated diffraction pattern of the monoclinic polymorph (VALIDL), is not. Figures S1 and S2 illustrate the process of identifying the DL-valine polymorph.

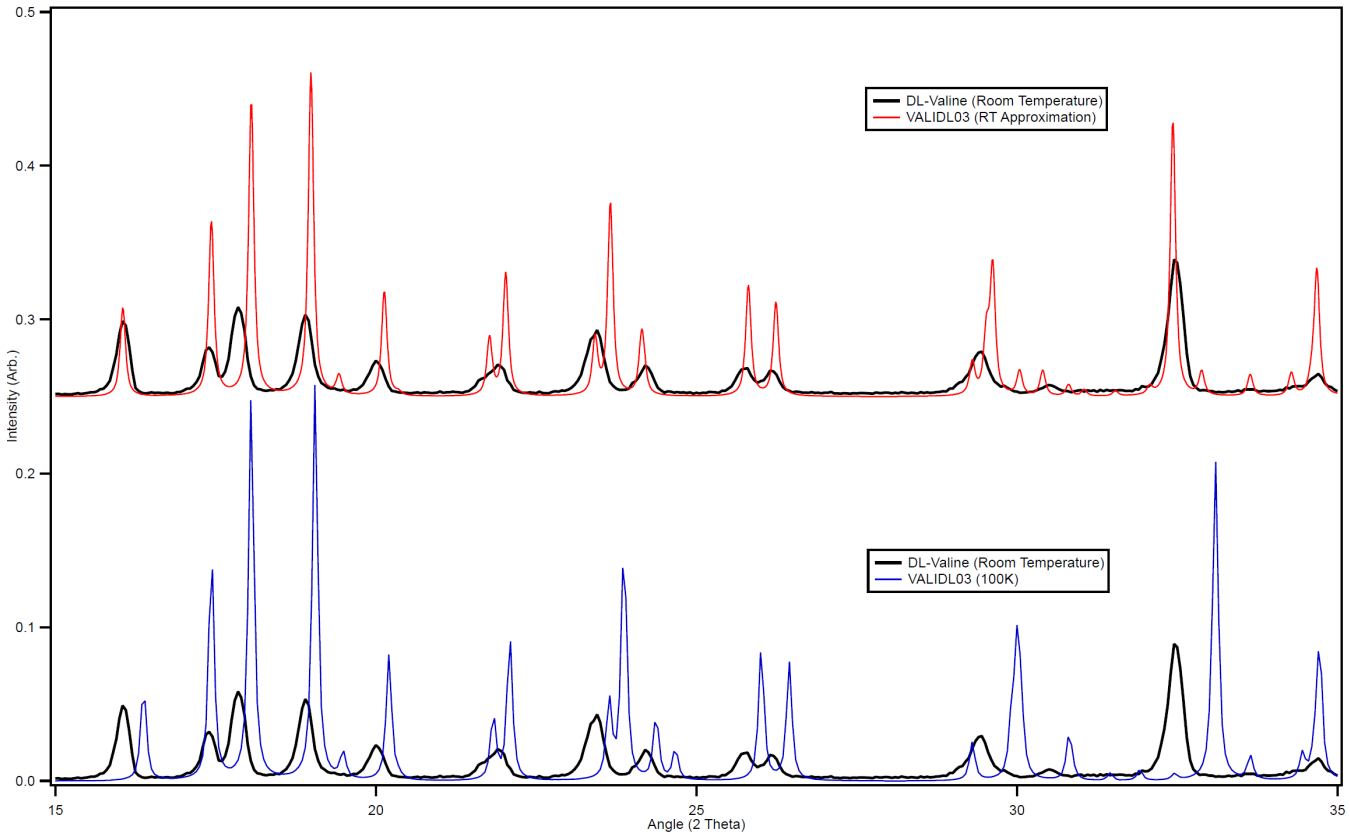

Figure S1. Low temperature crystallographic coordinates of the triclinic form of DL-valine (VALIDL03) do not initally result in a calculated diffraction pattern in accord with our room temperature powder XRD data (bottom). However, after simply scaling the unit cell of VALIDL03 to room temperature values, the calculated pattern is in

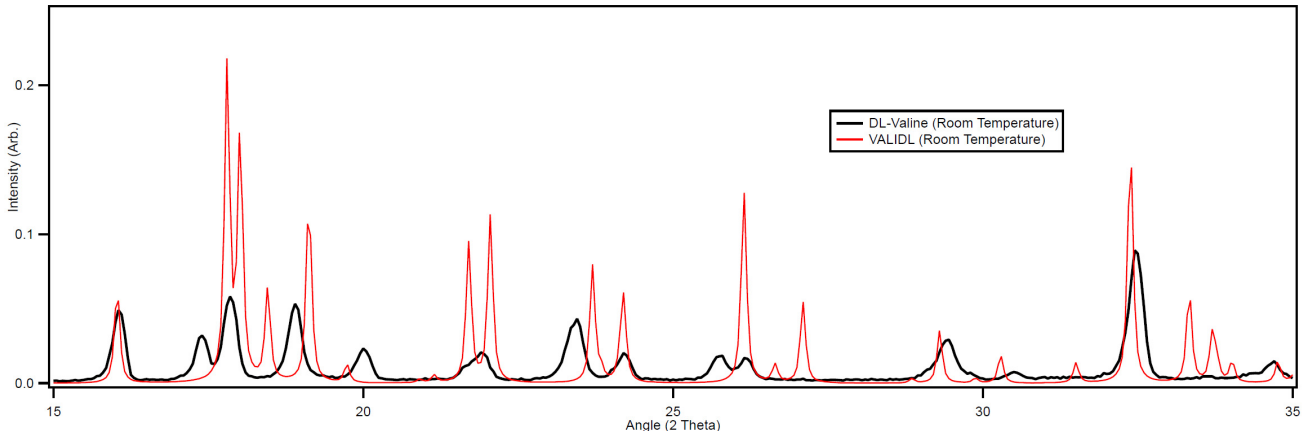

Figure S2. The calculated powder pattern of the monoclinic form of DL-valine (VALIDL) agrees poorly with our data. Unlike VALIDL03, the VALIDL coordinates were obtained at room temperature, and are therefore compared directly with the experimental powder XRD pattern.

III. Quantified Character of Motion for Low-Frequency Vibrational Modes in DL-Valine and L-Valine Crystal Systems

DL-valine 3-21G	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	1.45	46.52	53.48	39.88	13.60
2	1.97	17.28	82.72	60.81	21.91
3	2.04	60.98	39.02	0.01	39.01
4	2.76	36.73	63.27	19.01	44.26
5	3.34	63.32	36.68	0.01	36.67
6	3.51	70.78	29.22	25.30	3.92
7	4.00	63.63	36.37	12.46	23.91
8	4.32	69.86	30.14	8.89	21.25
9	4.48	75.86	24.14	0.01	24.13
10	4.99	74.90	25.10	13.72	11.38
11	5.13	99.02	0.98	0.00	0.98
12	6.43	89.13	10.87	1.76	9.11
13	6.93	95.21	4.79	0.00	4.79
14	7.03	87.70	12.30	1.34	10.96
15	7.10	84.72	15.28	0.00	15.27
16	7.98	94.78	5.22	0.12	5.10
17	8.23	92.55	7.45	0.02	7.44
18	9.18	98.44	1.56	0.02	1.53
19	9.81	95.41	4.59	0.02	4.57
20	10.01	99.61	0.39	0.04	0.35

DL-valine 6-31G	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	1.09	36.75	63.25	34.01	29.24
2	1.35	35.31	64.69	0.01	64.68
3	1.62	11.21	88.79	56.94	31.85
4	2.20	22.55	77.45	27.56	49.89
5	2.77	66.57	33.43	30.32	3.12
6	3.11	70.41	29.59	0.01	29.59
7	3.57	73.34	26.66	6.72	19.93
8	3.74	77.88	22.12	0.01	22.12
9	3.82	45.31	54.69	6.17	48.51
10	4.56	75.43	24.57	16.67	7.90
11	4.83	99.94	0.06	0.00	0.06
12	5.77	79.79	20.21	0.95	19.26
13	6.10	75.51	24.49	0.01	24.48
14	6.34	92.56	7.44	2.15	5.30
15	6.39	95.76	4.24	0.02	4.22
16	7.24	99.82	0.18	0.10	0.08
17	7.26	99.38	0.62	0.01	0.61
18	8.35	97.54	2.46	0.09	2.37
19	8.75	96.54	3.46	0.00	3.45
20	9.01	99.93	0.07	0.03	0.04

DL-valine 6-31G*	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	1.09	37.10	62.90	43.26	19.64
2	1.44	36.86	63.14	0.00	63.14
3	1.54	16.89	83.11	51.28	31.83
4	2.02	21.38	78.62	23.09	55.53
5	2.70	65.90	34.10	30.91	3.18
6	3.02	69.53	30.47	0.01	30.47
7	3.55	58.17	41.83	8.03	33.80
8	3.74	74.80	25.20	5.89	19.31
9	3.84	76.03	23.97	0.02	23.95
10	4.59	75.11	24.89	15.33	9.56
11	4.66	99.77	0.23	0.01	0.22
12	5.77	81.74	18.26	1.19	17.06
13	6.04	75.61	24.39	0.01	24.39
14	6.24	91.77	8.23	2.32	5.91
15	6.38	96.27	3.73	0.00	3.72
16	7.24	99.31	0.69	0.16	0.53
17	7.28	99.41	0.59	0.02	0.57
18	8.28	98.01	1.99	0.08	1.91
19	8.71	96.73	3.27	0.01	3.26
20	9.31	99.80	0.20	0.04	0.16

DL-valine 6-31G**	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	1.07	38.43	61.57	42.61	18.96
2	1.35	37.09	62.91	0.01	62.91
3	1.53	18.84	81.16	48.93	32.23
4	1.98	41.39	58.61	26.55	32.06
5	2.67	66.14	33.86	30.10	3.75
6	2.99	65.44	34.56	0.01	34.55
7	3.52	56.74	43.26	7.28	35.98
8	3.67	73.96	26.04	6.00	20.05
9	3.80	76.66	23.34	0.02	23.31
10	4.44	76.01	23.99	15.18	8.81
11	4.60	99.65	0.35	0.00	0.34
12	5.59	79.32	20.68	0.54	20.14
13	5.89	75.29	24.71	0.00	24.71
14	6.14	93.15	6.85	1.95	4.90
15	6.29	95.87	4.13	0.01	4.12
16	7.21	99.53	0.47	0.18	0.28
17	7.24	99.31	0.69	0.03	0.66
18	8.20	98.17	1.83	0.03	1.80
19	8.60	97.61	2.39	0.01	2.39
20	9.19	99.84	0.16	0.02	0.14

DL-valine 6-31G** Fixed Cell	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	1.70	37.90	62.10	0.01	62.10
2	1.74	16.29	83.71	82.42	1.29
3	2.18	26.88	73.12	1.18	71.94
4	2.37	13.44	86.56	76.96	9.60
5	3.15	58.70	41.30	0.01	41.29
6	3.17	77.32	22.68	21.36	1.32
7	3.93	68.59	31.41	16.39	15.02
8	4.05	43.97	56.03	1.74	54.29
9	4.37	77.90	22.10	0.01	22.09
10	4.59	73.66	26.34	16.04	10.29
11	4.88	95.51	4.49	0.00	4.49
12	5.94	82.26	17.74	0.47	17.27
13	6.23	79.41	20.59	0.01	20.57
14	6.43	94.57	5.43	0.01	5.42
15	6.48	93.49	6.51	1.48	5.03
16	7.45	99.21	0.79	0.22	0.57
17	7.71	99.10	0.90	0.05	0.85
18	8.39	98.22	1.78	0.01	1.77
19	8.70	98.05	1.95	0.00	1.95
20	9.50	99.69	0.31	0.16	0.15

L-valine 6-31G**	Freq (THz)	Intramolecular (%)	Total Intermolecular (%)	Translational Intermolecular (%)	Rotational Intermolecular (%)
1	0.87	15.17	84.83	73.50	11.33
2	1.32	24.91	75.09	62.97	12.12
3	1.37	48.70	51.30	20.78	30.52
4	1.67	53.11	46.89	12.44	34.45
5	1.73	41.10	58.90	47.95	10.95
6	1.79	38.78	61.22	36.25	24.97
7	1.96	20.17	79.83	47.79	32.04
8	2.39	69.74	30.26	3.15	27.11
9	2.43	22.24	77.76	20.63	57.13
10	2.63	89.32	10.68	8.21	2.47
11	2.71	80.33	19.67	5.81	13.87
12	2.76	52.37	47.63	43.17	4.45
13	2.79	70.72	29.28	22.75	6.53
14	2.95	58.32	41.68	5.60	36.09
15	3.13	71.01	28.99	5.02	23.97
16	3.16	50.44	49.56	4.01	45.55
17	3.28	70.67	29.33	2.41	26.92
18	3.60	71.67	28.33	1.38	26.95
19	3.61	70.53	29.47	2.58	26.89
20	3.91	78.05	21.95	10.49	11.47
21	4.00	87.91	12.09	5.57	6.52
22	4.34	58.99	41.01	32.28	8.73
23	4.59	78.90	21.10	11.62	9.49
24	4.63	80.48	19.52	4.54	14.98
25	4.85	65.86	34.14	7.08	27.06
26	5.02	73.54	26.46	4.05	22.41
27	5.30	73.56	26.44	5.19	21.25
28	5.65	89.21	10.79	8.68	2.11
29	5.74	68.74	31.26	5.53	25.74
30	6.10	97.14	2.86	1.46	1.40
31	6.28	95.73	4.27	3.45	0.82
32	6.39	97.66	2.34	1.91	0.43
33	6.51	84.04	15.96	7.83	8.13
34	6.55	92.86	7.14	2.91	4.22
35	6.85	93.69	6.31	2.93	3.38
36	6.87	99.63	0.37	0.21	0.17
37	6.88	99.09	0.91	0.36	0.55
38	7.57	99.41	0.59	0.09	0.50
39	7.72	98.45	1.55	0.47	1.08
40	8.19	99.33	0.67	0.33	0.33

IV. Movie Files

Animations of vibrational modes discussed in the article are available here in the animated .gif format, which allows convenient viewing of several modes at a time. The files are named in the following manner:

{compound}_{basis set}_{mode number}_{unit cell vector}.gif

Where the unit cell vector refers to the direction along which one is viewing the molecules in a particular animation. For example, the file "dlval_631G_nu8_b.gif" is an animation of the eighth vibrational mode calculated for DL-valine using the 6-31G basis set and viewed along unit cell vector b. Note that since the * character is not allowed in file names, the other common designation for basis sets is used. Specifically, 6-31G(d) is the same as 6-31G*, and 6-31G(d,p) is the same as 6-31G**.

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