Electronic Supplementary Information
Exploring the solid state phase transition in DL-norvaline with terahertz spectroscopy

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DOI: 10.1039/b000000x

Electronic Supplementary Information

1 Justification of Approximation in eq (2)

In equation (2) of the main text, we approximated that the total phase delay is caused by the real component of the refractive index of the pellet through which the THz wave propagates. However, when an absorbing medium is involved, there is also a phase shift at the interfaces. This contribution can be neglected due to the weak absorption of the pellets because the phase phase shift due to $t_{12}(\omega)$ and $t_{21}(\omega)$ is negligible compared to the phase propagation term.

Even at the absorption maximum at 1.55 THz, the imaginary part is roughly 0.025. The contribution to the phase change is more than 8000 times smaller than the phase change due to propagation through a 3 mm thick pellet with a refractive index of about 1.6. To illustrate this, we plotted the phase delay, at 1 THz caused by a 3 mm pellet with a refractive index of 1.6 in Fig. S1, blue line. The additional contribution from the complex transmission coefficients, $t_{12}(\omega)$ and $t_{21}(\omega)$, is plotted in red. The relative difference is less than 0.02%. Therefore, the approximation in eq. (2) in the main text is valid for mixed pellets that contain $\approx 2\%$ amino acid. We would like to stress, that a thin layer of highly absorbing material cannot be approximated in the same way, and this is an additional advantage of using Teflon/amino acid pellets rather than pressing free standing pure amino acid pellets.

2 Sample Mixtures

Table S1 shows the mixing ratio for the pellets presented in this paper. Accurate mixing ratios are required when using the Bruggeman equation to calculate the permitivitty of the crystallites, and from this the absorption coefficient.

3 Calculated Terahertz Spectra

The IR spectrua of all possible conformer combinations are plotted together with the experimental results in Fig. S2 and Fig. S3. The naming system of these conformers is explained in the main text.

4 Mode chart

Using the method discussed in the main paper[1], we calculated the mode character of the different resonances for all six conformers. The results are plotted in Fig. S4.

5 Structure of used Amino Acids

The molecular structures of DL-norvaline, and all dopants used are plotted in Fig. S5

6 PXRD Characterication of the Grown Crystals

The crystals where characterized via PXRD. The spectra are plotted in Fig. S6 and Fig. S7. These spectra are used to distinguish between doped and mixed crystals.

References

1 Neu, J.; Nemes, C.T. ; Regan, K.P. ; Williams, M.R.C. ; Schmuttenmaer, C.A *PCCP* **2017**, *00*, 000 – 000.

Material	amino acid [mg]	Teflon [mg]	Thickness [mm]	Figure (in main text)
pure DL-Nva	43	1014	3.39	Fig 1 and Fig 2
DL-Nva:L-Glu	33	1060	3.54	Fig 8
DL-Nva:L-P.	24	1060	3.54	Fig 9
DL-Nva:L-P.:D-P.	27	1046	3.49	Fig 10
pure DL-Nva 5 µm	20	1014	3.39	Fig 5
pure DL-Nva 125 µm $< s <$ 250 µm	22	1059	3.54	Fig 6

Table S1 Mixing rates of the presented samples. With, DL-Nva as acronym for DL-norvaline, L-Glu for L-glutamic acid, L-P. for L-phenylglycine and D-P. for L-phenylglycine and D-phenylglycine.

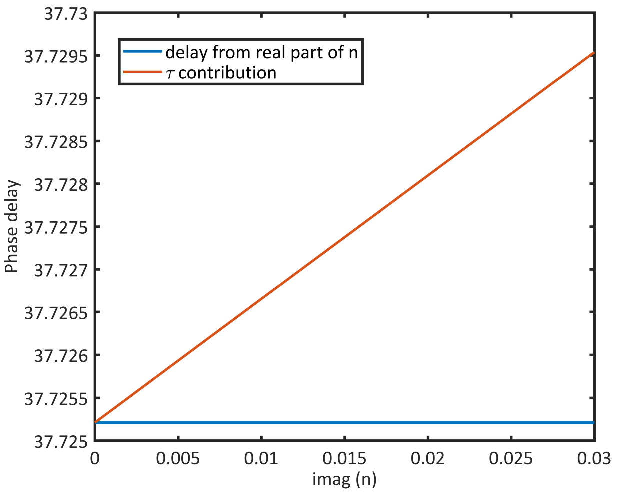

Fig. S1 Approximation of the phase change caused by the complex Fresnel coefficients $t_{12}(\omega)$ and $t_{21}(\omega)$. The resulting error for the situation in which the imaginary part is 0.03 is still less than 0.02%.

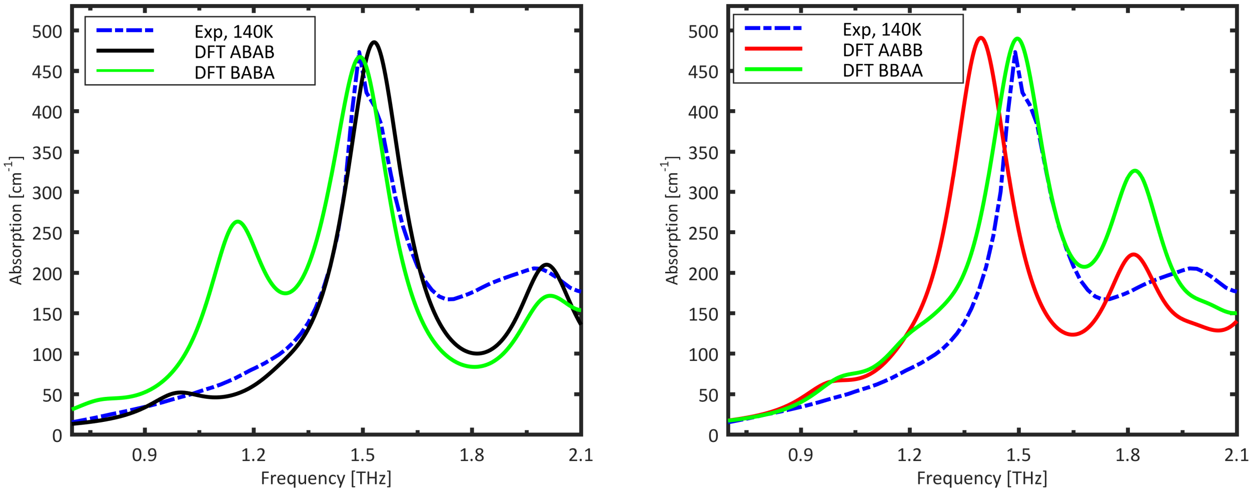

Fig. S2 Simulated absorption spectra for DL-norvaline. The simulated data are normalized to ensure that the primary absorption peak is superposed with the experimental results. The calculated frequencies and intensities are convoluted with a Lorentz function with FWHM of 0.2 THz.

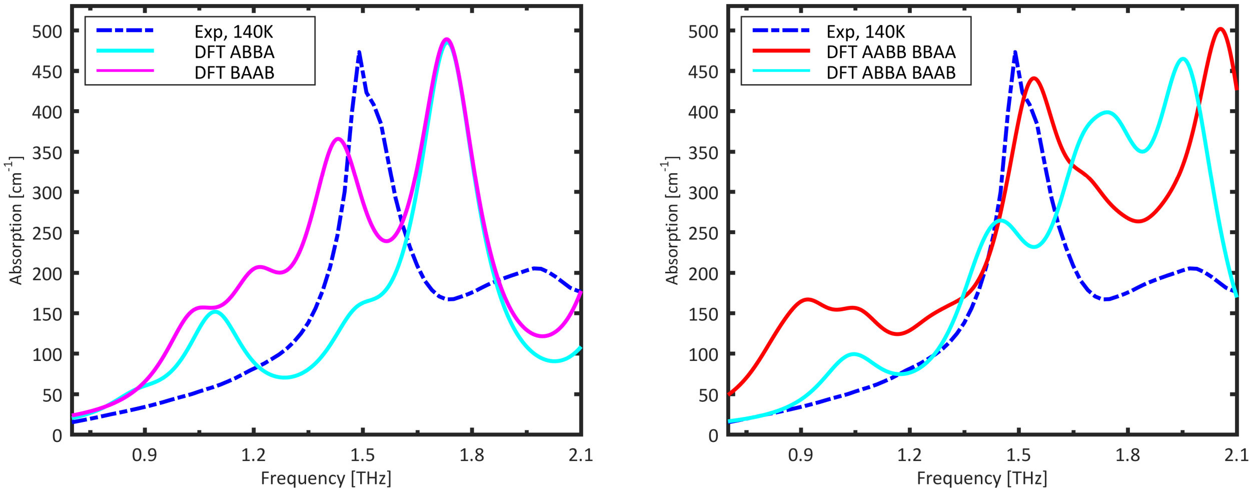

Fig. S3 Simulated absorption spectra for DL-norvaline. The simulated data are normalized to ensure that the primary absorption peak is superposed with the experimental results. The calculated frequencies and intensities are convoluted with a Lorentz function with FWHM of 0.2 THz. The right-hand plot displays the results for a calculation performed on a 8 molecule supercell.

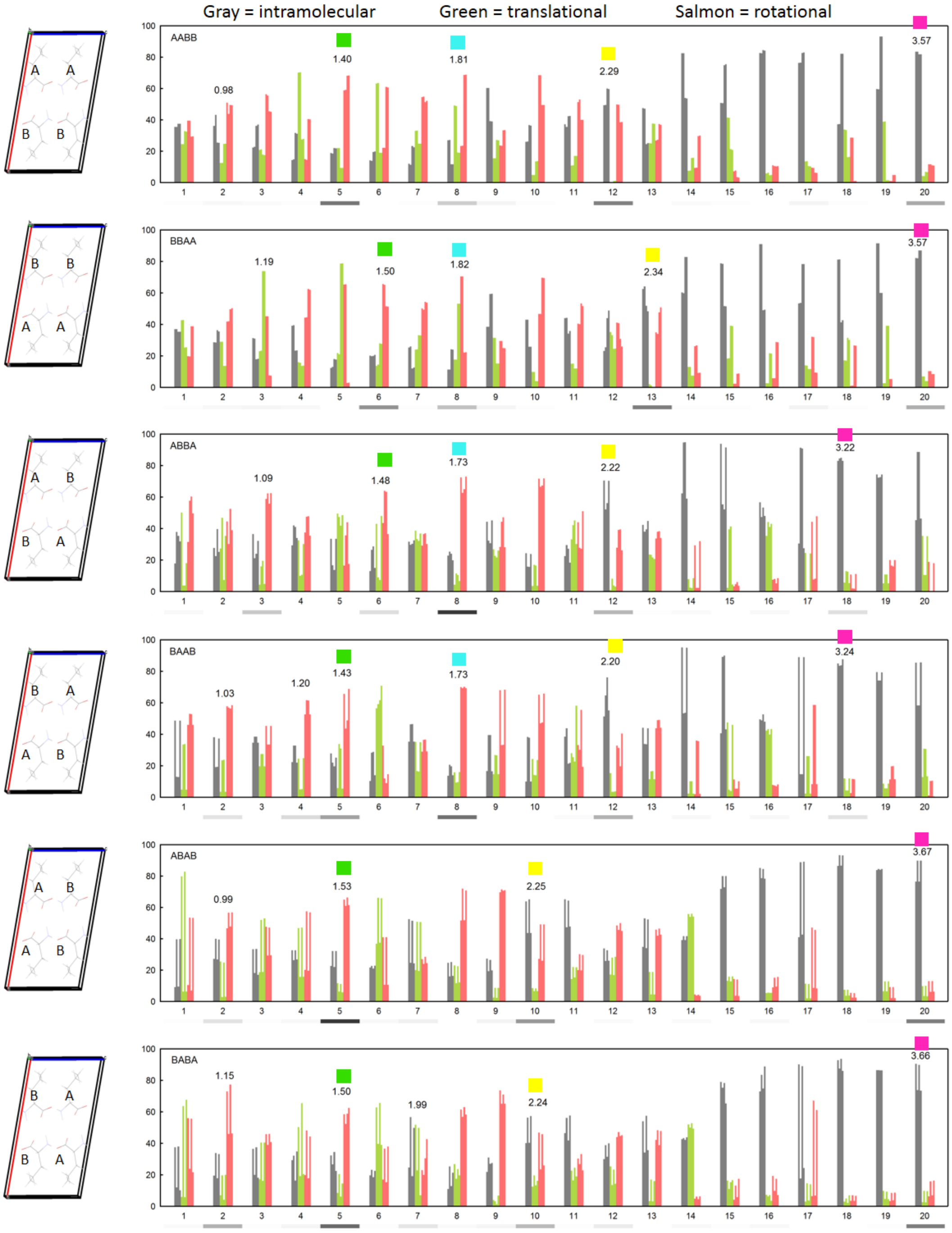

Fig. S4 Mode characters of the IR-active modes from the calculations. The mode located closes to the experimental resonance is marked with a cyan square.

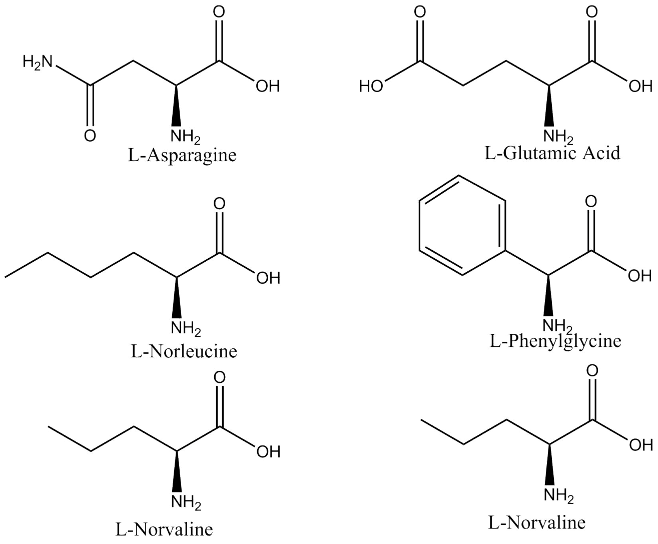

Fig. S5 Chemical structure of the amino acids used.

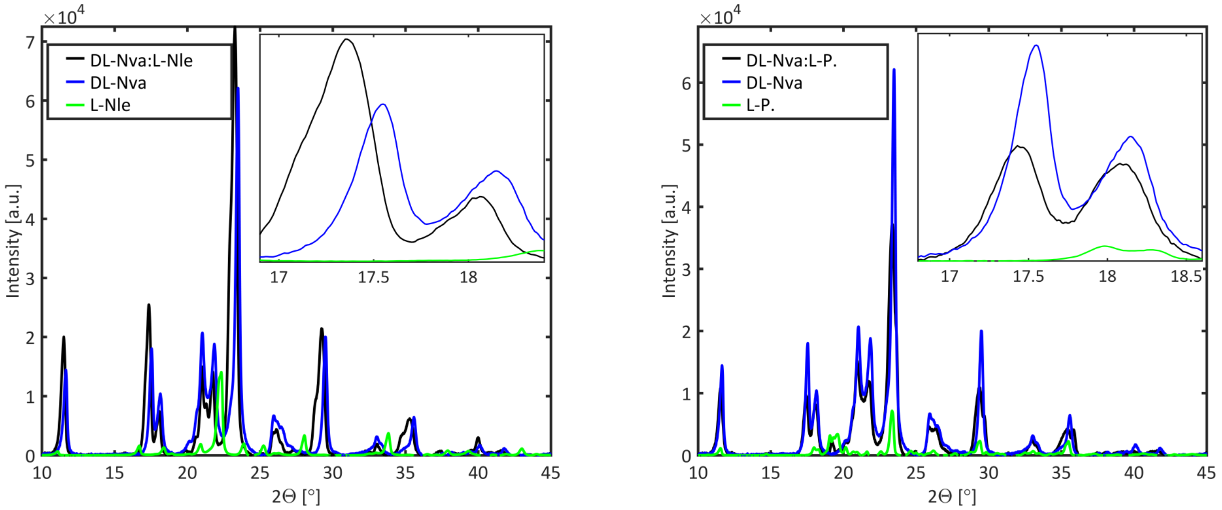

Fig. S6 Powder XRD of a crystal grown out of (a) a mixture of 12mol% DL-Norleucine in DL-norvaline and (b) a mixture of 12mol% L-phenylglycine in DL-norvaline.

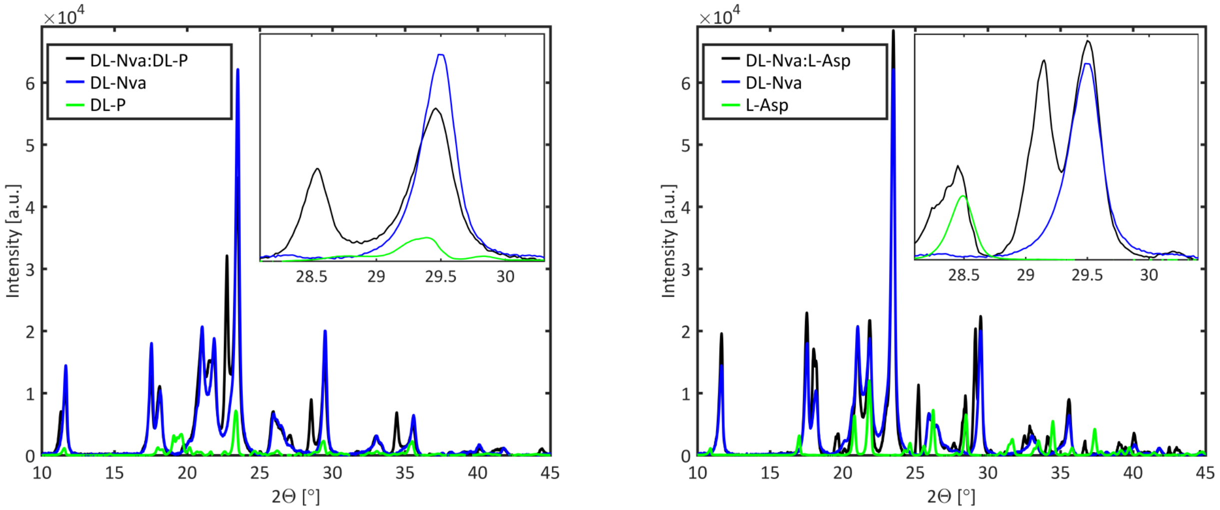

Fig. S7 Powder XRD of a crystal grown out of (a) a mixture of 12mol% L-phenylglycine and D-phenylglycine in DL-norvaline and (b) a mixture of 12mol% L-asparagine in DL-norvaline.