

Supporting information for

**The accuracy of carbon-13 NMR magnetic-shielding tensors  
calculated by periodic DFT: Case study on the distinction of  
crystalline serine phases**

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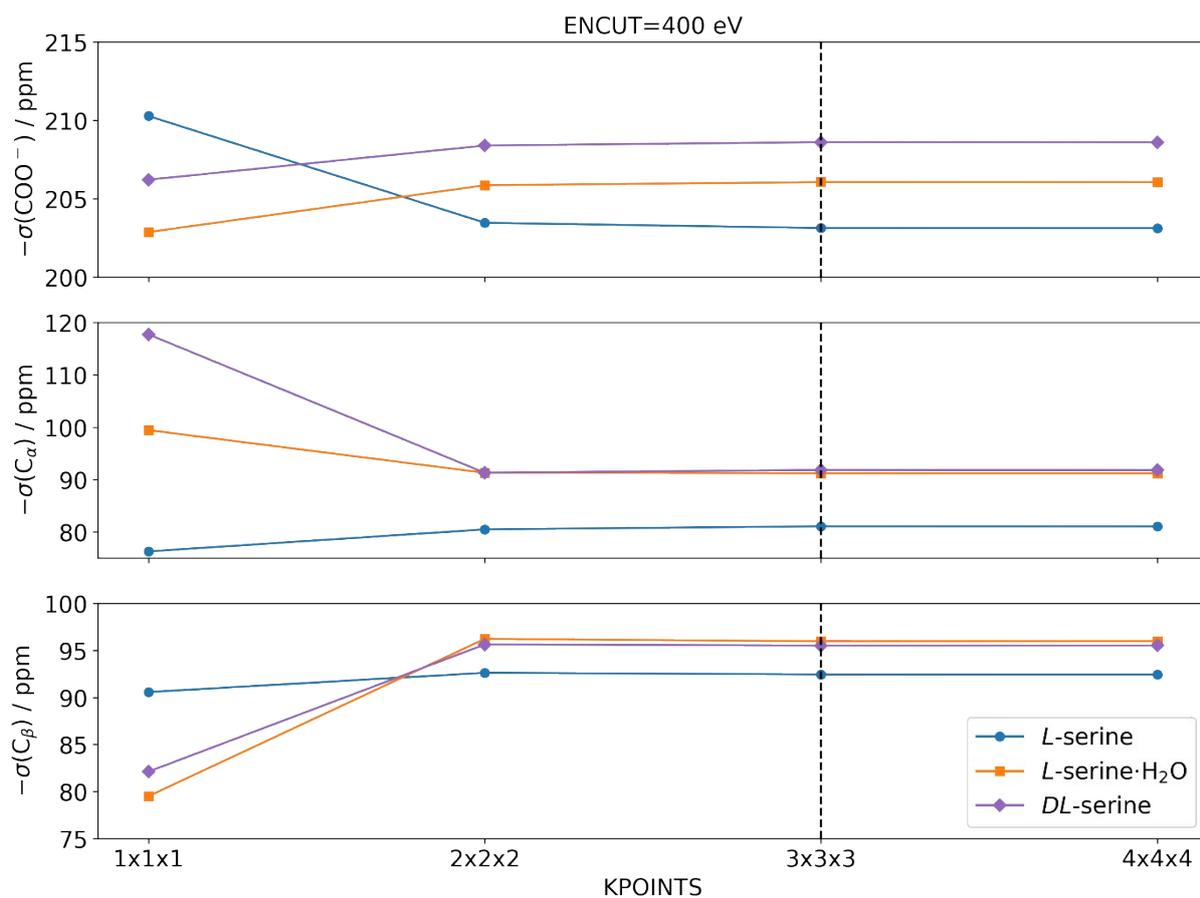
## 1. EXPERIMENTAL AND COMPUTATIONAL DETAILS

**Table S1:** Experimental solid-state NMR parameters of the performed  $^1\text{H}$ - $^{13}\text{C}$  CP MAS experiments at a 11.7 T spectrometer.

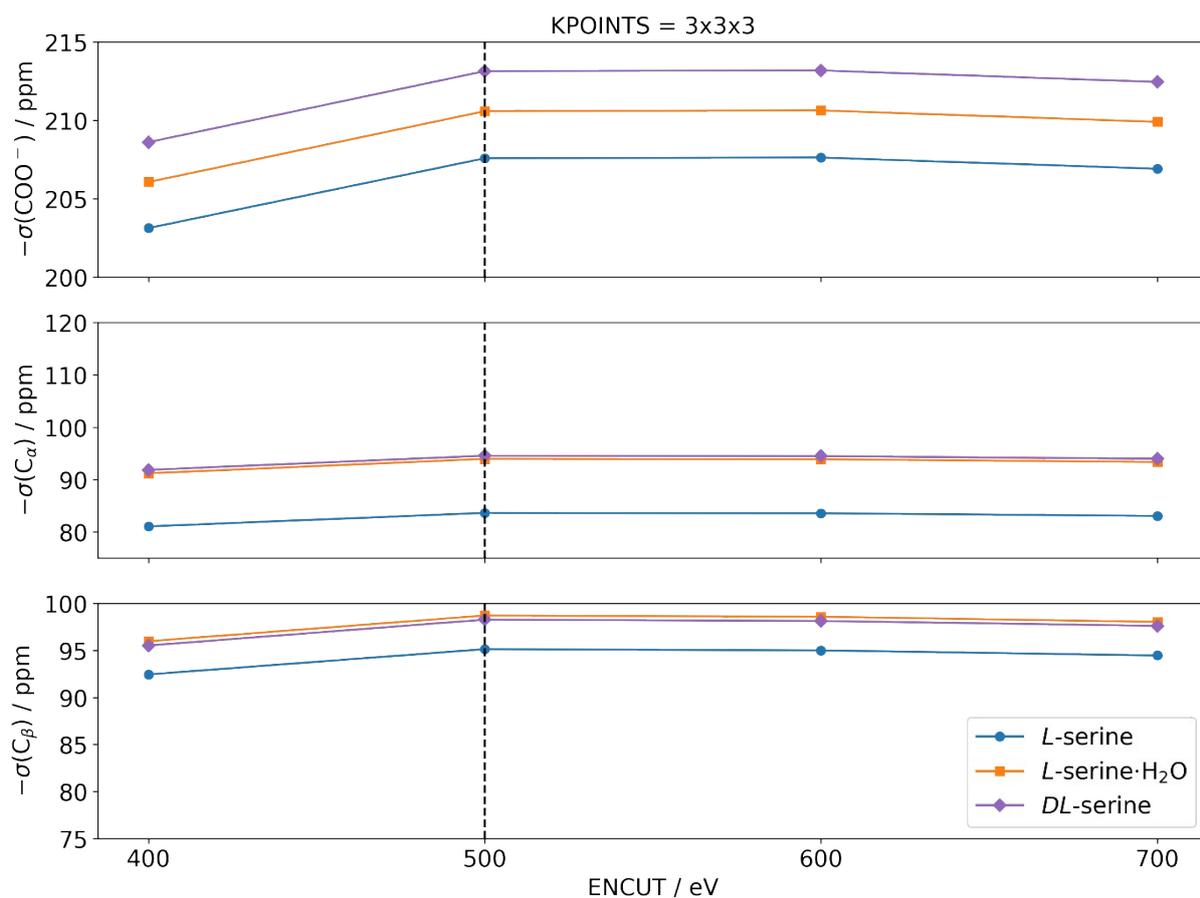
<b>Experiment</b>	<b><math>^1\text{H}</math>-<math>^{13}\text{C}</math> CP-MAS</b>	
$\nu_r$ / kHz	17.0	2.0
$B_0$ / T	11.7	
<b>CP polarization Transfer</b>	<b>H-C CP</b>	
$\nu_1(^1\text{H})$ / kHz	61.3	53.7
$\nu_1(^{13}\text{C})$ / kHz	44.6	47.4
<b>Shape</b>	Tangent shape	
$^{13}\text{C}$ carrier/ ppm	100	
<b>CP contact time</b> / $\mu\text{s}$	1500	1000
<b>Sweep width</b> / ppm	795	
<b>Acquisition time</b> / ms	25.6	
<b><math>^1\text{H}</math> Spinal64 decoupling</b> / kHz	90	
<b>Interscan delay</b> / s	90	
<b>Probe target temperature</b> / K	285	

**Table S2:** Experimental solid-state NMR parameters of the performed  $^1\text{H}$ - $^{13}\text{C}$  CP MAS experiments at a 16.4 T spectrometer.

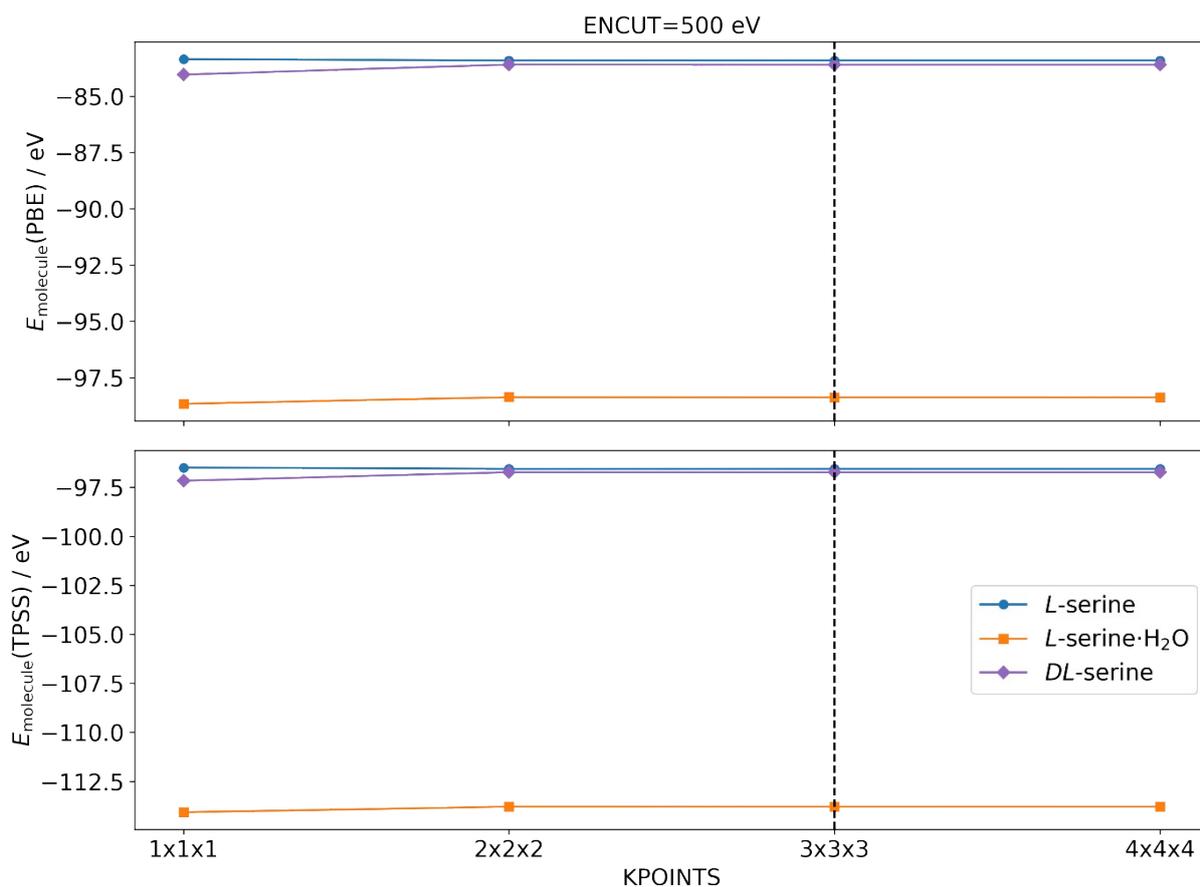
<b>Experiment</b>	<b><math>^1\text{H}</math>-<math>^{13}\text{C}</math> CP-MAS</b>
$\nu_r$ / kHz	2.0
$B_0$ / T	16.4
<b>CP polarization Transfer</b>	<b>H-C CP</b>
$\nu_1(^1\text{H})$ / kHz	55.1
$\nu_1(^{13}\text{C})$ / kHz	44.0
<b>Shape</b>	Tangent shape
$^{13}\text{C}$ carrier/ ppm	100
<b>CP contact time</b> / $\mu\text{s}$	1000
<b>Sweep width</b> / ppm	567.8
<b>Acquisition time</b> / ms	25.6
$^1\text{H}$ Spinal64 decoupling/ kHz	90
<b>Interscan delay</b> / s	90
<b>Probe target temperature</b> / K	285



**Figure S1:** Overview of initial benchmarks for computing isotropic  $^{13}\text{C}$  magnetic shielding-values with a constant kinetic energy cutoff of 400 eV in VASP. Magnetic-shielding values of  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{COO}^-$  were calculated without prior optimization of hydrogen atom positions. The k-point mesh was gradually increased until convergence at a regular  $3 \times 3 \times 3$  k-point mesh was observed, highlighted by the dashed vertical lines.

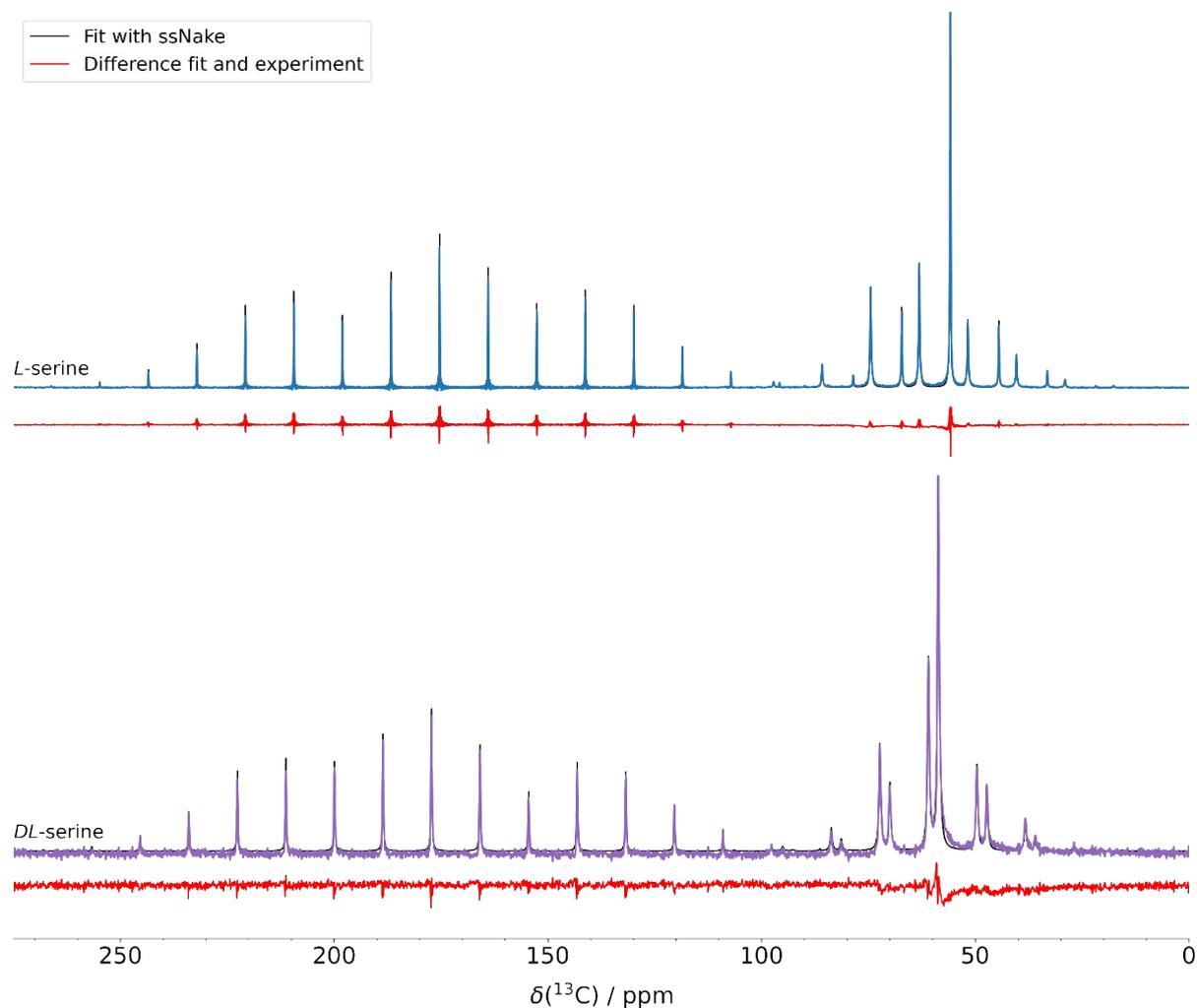


**Figure S2:** Overview of initial benchmarks for computing  $^{13}\text{C}$  magnetic shielding-values with a constant regular 3x3x3 k-point mesh in VASP. Magnetic-shielding values of  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{COO}^-$  were calculated without prior optimization of hydrogen atom positions. The kinetic energy cutoff was gradually increased until convergence at 500 eV was observed, highlighted by the dashed vertical lines.



**Figure S3:** Overview of initial benchmarks for the geometry optimization of hydrogen-atom positions using the PBE GGA-functional and TPSS meta-GGA-functional in VASP. The same kinetic energy cutoff of 500 eV as for the computation of  $^{13}\text{C}$  isotropic magnetic shielding-values (see Figure S2) was chosen and kept constant during the benchmarks. The plots show the optimized energy per molecule as a function of the k-point mesh. Convergence was achieved at a regular 3x3x3 k-point mesh.

## 2. SOLID-STATE NMR SPECTRA



**Figure S4:**  $^1\text{H}$ - $^{13}\text{C}$  CP-MAS NMR slow-spinning spectra of *DL*-serine (purple) and *L*-serine (blue) recorded at 16.4 T and 2.0 kHz MAS. Lineshape simulations are shown as black lines. Differences between experiment and fit are shown in red as difference spectrum.

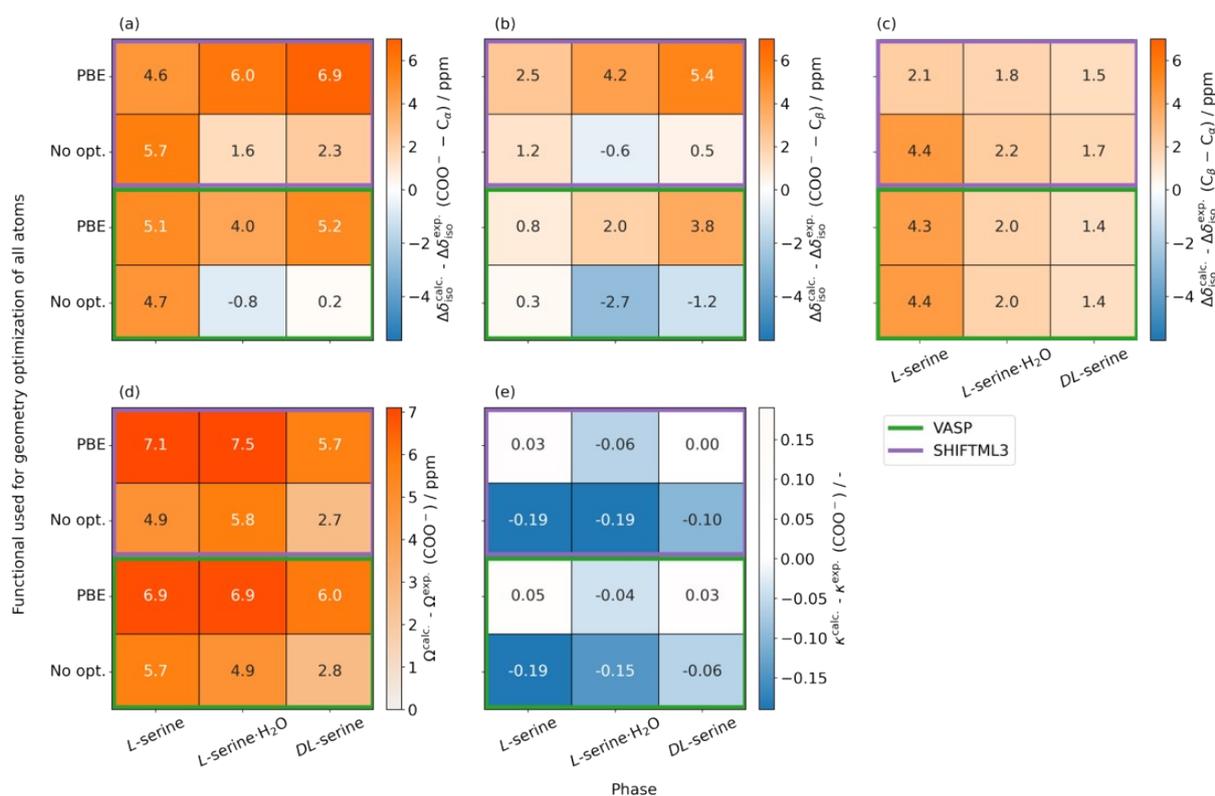
**Table S3:** Overview of experimentally determined  $^{13}\text{C}$  CSA parameters (11.7 T) for the  $\alpha$ -carbon of the three serine phases. In brackets the values determined from the spectra recorded at 16.4 T are reported.

	$\Omega^{exp.}(C_\alpha) / \text{ppm}$	$\kappa^{exp.}(C_\alpha)$
<i>L</i> -serine	31.4 [30.2]	0.3 [0.2]
<i>L</i> -serine $\cdot$ H <sub>2</sub> O	30.8 [-]	0.2 [-]
<i>DL</i> -serine	32.7 [29.7]	0.2 [0.04]

**Table S4:** Overview of experimentally determined  $^{13}\text{C}$  CSA parameters (11.7 T) for the  $\beta$ -carbon of the three serine phases. In brackets the values determined from the spectra recorded at 16.4 T are reported.

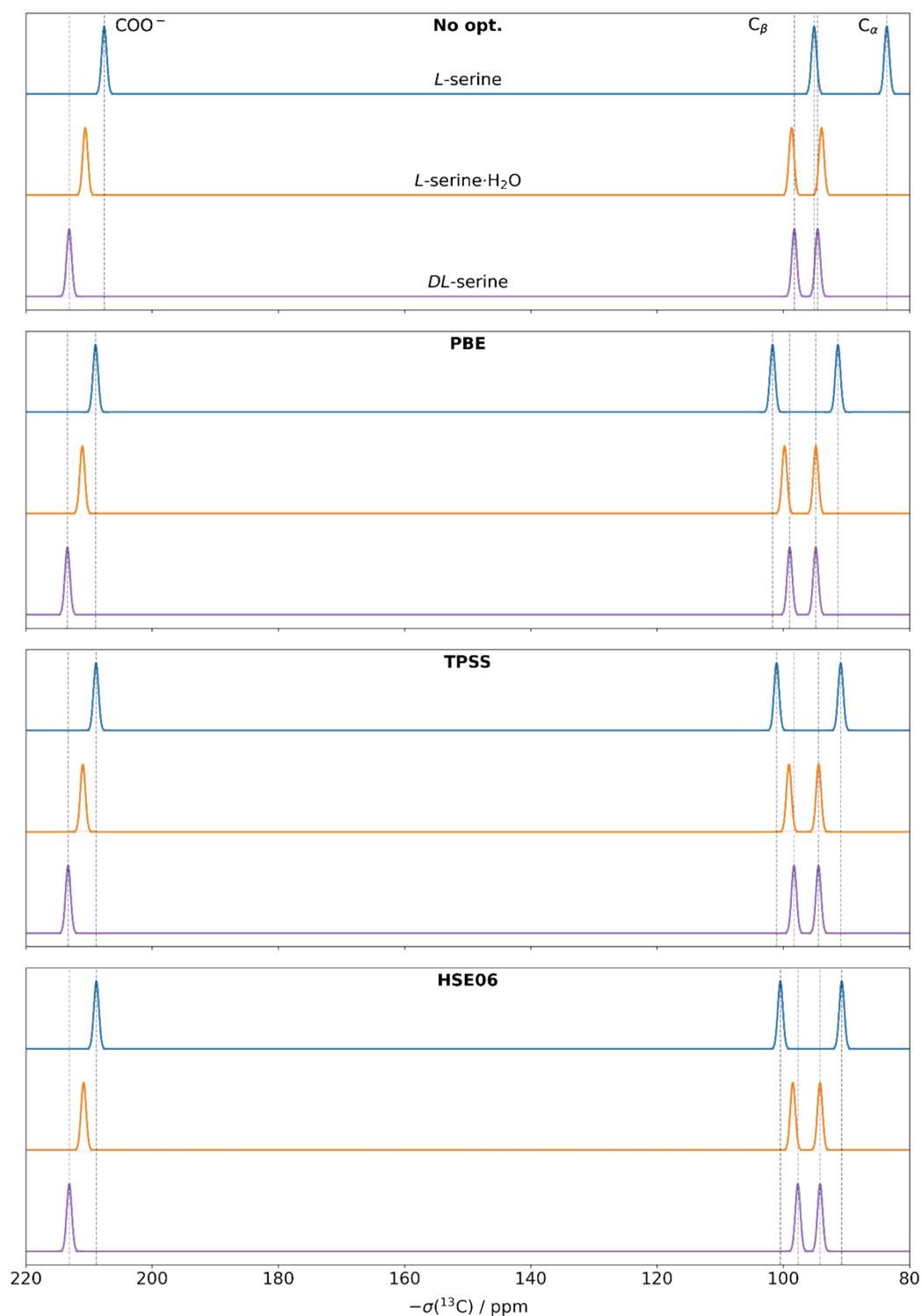
	$\Omega^{\text{exp.}}(C_{\beta}) / \text{ppm}$	$\kappa^{\text{exp.}}(C_{\beta}) / -$
<i>L</i> -serine	54.2 [53.6]	0.3 [0.3]
<i>L</i> -serine $\cdot$ H <sub>2</sub> O	48.7 [-]	0.3 [-]
<i>DL</i> -serine	48.9 [47.3]	0.2 [0.2]

### 3. COMPARISON OF EXPERIMENTAL AND THEORETICAL NMR PARAMETERS AFTER FULL GEOMETRY OPTIMIZATION

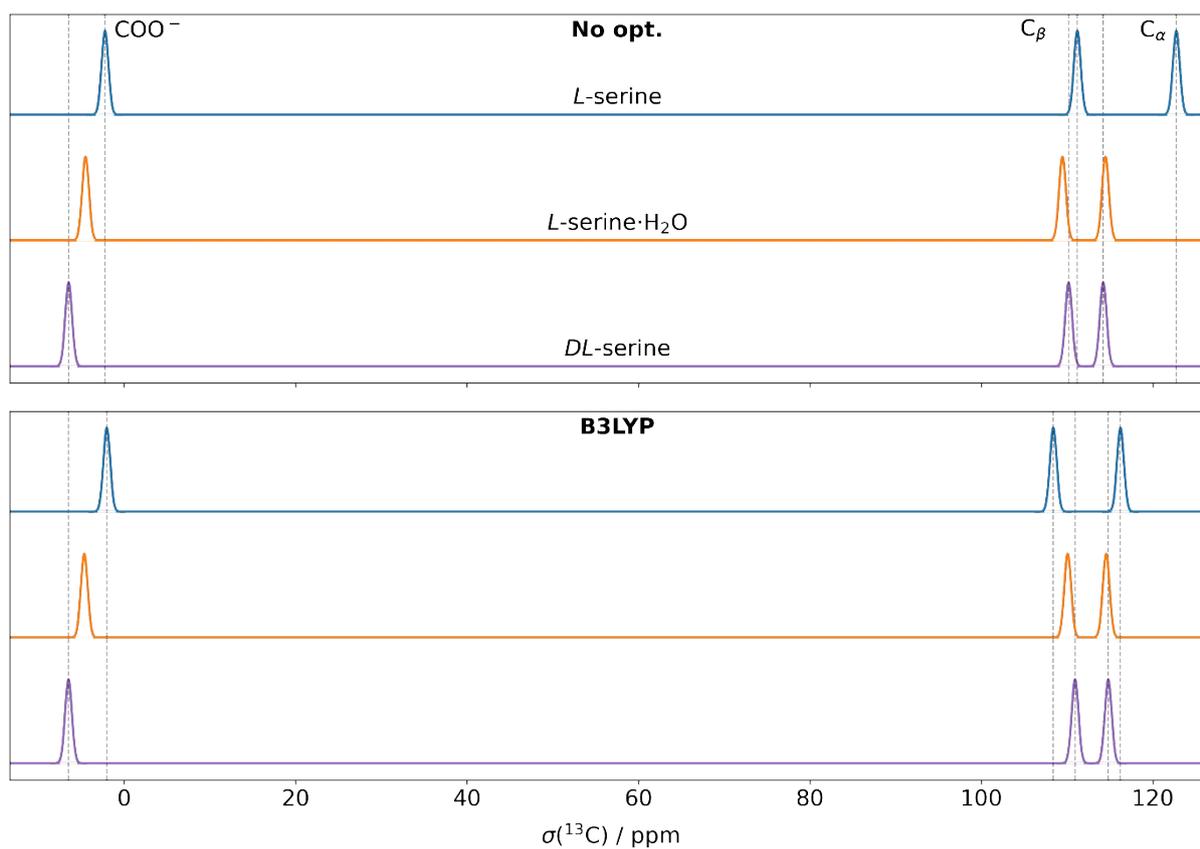


**Figure S5:** “Heat maps” comparing experimental and DFT-calculated isotropic  $^{13}\text{C}$  chemical-shift values. Prior to the calculation of  $^{13}\text{C}$  magnetic-shielding tensors, the positions of all atoms were optimized in VASP employing a PBE level-of-theory and compared to the case where no prior optimization was performed (no opt.). The differences between experimental and DFT-calculated values for the difference of the chemical-shift values between the carboxyl acid group carbon and  $\text{C}_{\alpha}$  (a), between the carboxyl acid group carbon and  $\text{C}_{\beta}$  (b) and between  $\text{C}_{\beta}$  and  $\text{C}_{\alpha}$  (c) for the three different serine phases are plotted in units of ppm. “Heat maps” of the CSA parameters  $\Omega$  (d) and  $\kappa$  (e) only for  $\text{COO}^-$ . In VASP (highlighted by the green lines) calculations of  $^{13}\text{C}$  magnetic-shielding tensors have been performed in all cases with the PBE DFT functional. As comparison and separated by the purple lines the results obtained by using the machine learning model ShiftML3 are shown.

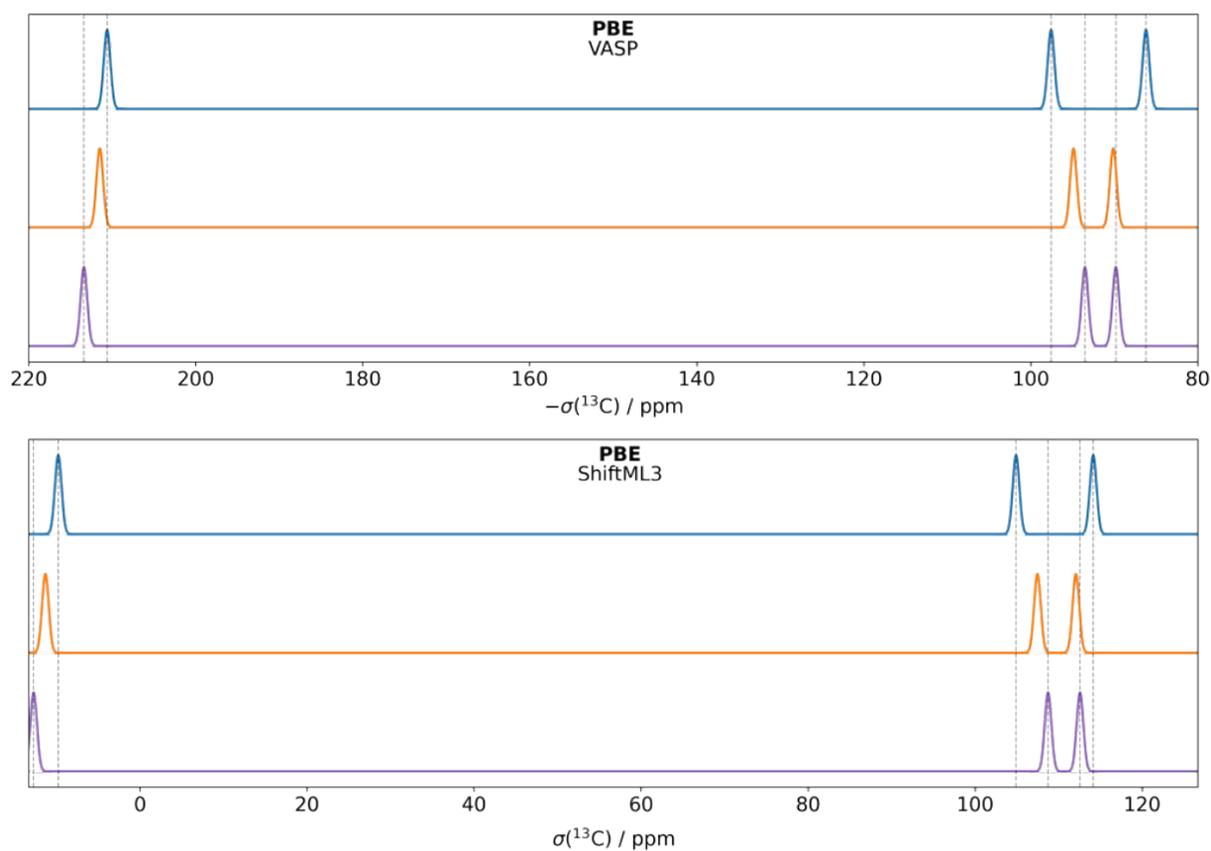
#### 4. SIMULATED SOLID-STATE NMR SPECTRA



**Figure S6:** Simulated  $^{13}\text{C}$  NMR-spectra using the calculated isotropic  $^{13}\text{C}$  magnetic-shielding values in VASP determined after optimizing the hydrogen atoms in VASP employing the different level-of-theory as indicated in bold. For visualization gaussian functions were used utilizing the calculated magnetic shielding values as expected values and a standard deviation of 0.4 ppm.



**Figure S7:** Simulated  $^{13}\text{C}$  NMR-spectra using the calculated isotropic  $^{13}\text{C}$  magnetic-shielding values from ShiftML3. Magnetic shielding values were calculated for the non-optimized crystal structures (no opt.) and for the crystal structures obtained after optimizing the H-atom positions in VASP on a B3LYP level-of-theory (B3LYP). For visualization gaussian functions were used utilizing the calculated magnetic shielding values as expected values and a standard deviation of 0.4 ppm.



**Figure S8:** Simulated  $^{13}\text{C}$  NMR spectra of *DL*-serine (purple, bottom), *L*-serine· $\text{H}_2\text{O}$  (orange, middle) and *L*-serine (blue, top) using the calculated isotropic  $^{13}\text{C}$  magnetic-shielding values from VASP determined after optimizing all atoms on a PBE level-of-theory (top). Calculated isotropic  $^{13}\text{C}$  magnetic-shielding values from ShiftML3 for the crystal structures obtained after optimization of all atoms on a PBE level-of-theory in VASP (bottom). For visualisation gaussian functions were used utilizing the calculated magnetic-shielding values as expected values and a standard deviation of 0.4 ppm. The dashed lines serve as guides to the eye.