

Supplementary material: High-pressure synthesis of acentric sodium pyrocarbonate, Na₂[C₂O₅]

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1. Methods

1.1. Sample material

For the high-pressure experiments we used commercial Na₂[CO₃] powder (99.99% purity, Merck, Darmstadt, Germany). First, the Na₂[CO₃] powder was dried in an oven at 573(1) K for 12 h. Afterwards, the powder was compacted between a diamond and a glass plate to obtain a 10–20 µm thin powder compact. We used the CO₂ gas for the gas-jet as purchased (Nippon gases, purity ≥ 99.995%).

1.2. High-pressure experiments

The high-pressure experiments were carried out using Boehler-Almax type diamond anvil cells (DACs) with 350 µm culet size and diamonds with 70° opening angle on both sides.¹ We used Re-gaskets which were pre-indented to a thickness of ≈ 45 µm. Gasket-holes with 120 µm diameter were drilled by a custom-built laser setup. First, the powder compact with dimensions of ≈ 80 × 50 µm² and a thickness of 10–20 µm was placed on the culet of the bottom diamond. Afterwards, we added a ruby chip for pressure determination in the gasket hole. The pressure was determined by measuring the shift of the ruby fluorescence and we assume an error of 6% due to non-hydrostatic conditions.²

CO₂ dry-ice was directly condensed into the gasket hole using a custom-built cryogenic loading system (see Spahr *et al.*³) derived from an earlier concept.⁴ The DAC was opened and placed on a liquid nitrogen cooled Cu-holder. It was cooled down to ≈ 100 K and Ar (10 l min⁻¹) was used as a purge-gas to avoid the precipitation of H₂O ice. We used a small nozzle to align the CO₂ gas jet with 5 l min⁻¹ directly on the gap between upper diamond and the gasket. The precipitation of the CO₂ in the gasket hole was monitored by an optical microscope and a camera. After a sufficient amount of CO₂ was gathered in the gasket hole, the DAC was tightly closed.

1.3. Raman spectroscopy and laser heating

High-pressure Raman spectroscopy and the double-sided laser-heating in DACs were performed using a custom-built set-up.⁵ Raman spectroscopy was performed with an Oxixus LCX-532S Nd:YAG laser (λ = 532.14 nm) in combination with a Princeton Instruments

ACTON SpectraPro (SP-2356) spectrograph equipped with a Pixis 256E CCD camera. Applying a laser power of 250 mW on the sample, the spot size of the Raman laser was ≈ 6 µm. Raman maps were measured on a grid with a step-size of 5 µm and the background was corrected using the software package Fityk.⁶

Double-sided laser-heating was performed using a Coherent Diamond K-250 pulsed CO₂ laser (λ = 10600 nm). The laser power was adjusted to achieve a coupling of the laser to the sample using a laser power of < 1 W. The sample was heated to the beginning of thermal radiation in the visible spectrum, which typically becomes visible at *T* ≈ 800 K.⁷ We assume that the highest temperature achieved during the laser heating was *T*_{max} ≈ 800(200) K. The temperatures were determined by the two-color pyrometer method, employing Planck and Wien fits.⁸ The heating time was ≈ 30 min. It is well established that laser-heating in DACs always suffers from large temperature gradients and the actual temperature is strongly dependent on the coupling of the laser with the sample, especially at lower temperatures. We estimate an uncertainty of at least ±10% of the nominal temperature in the laser-heated region depending on the focus of the laser beam, based on typical 2D temperature-gradient determination experiments performed in DACs.⁹

1.4. Single crystal synchrotron X-ray diffraction

Single crystal synchrotron X-ray diffraction was carried out at PETRA III (DESY) in Hamburg, Germany, at the extreme conditions beamline P02.2.¹⁰ The beam size on the sample was 2.2 (H) × 1.9 (V) µm² (FWHM), focused by Kirkpatrick Baez mirrors. The diffraction data were collected using a Perkin Elmer XRD1621 detector, a wavelength of 0.2906 Å (42.7 keV) and a detector to sample distance of 402 mm, calibrated from the powder diffraction of a CeO₂ standard and using the software DIOPTAS.¹¹ We rotated the DAC by ±34° around the axes perpendicular to the beam while collecting frames in 0.5° steps with 4 s acquisition time per frame. The diffractometer/detector geometry was calibrated using diffraction data collected from a single crystal of enstatite (MgSiO₃) in a DAC. After the data collection, the reflections were indexed and integrated employing CrysAlis^{PRO} (version 41.122a).¹² We used the Domain Auto Finder program (DAFi) to find possible single crystal domains for the

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subsequent data reduction.¹³ The structure solution and refinement were performed using the software package JANA2006 employing SHELXT for the crystal structure determination.^{14,15}

1.5. Second harmonic generation measurements

Second harmonic generation (SHG) measurements on $\text{Na}_2[\text{C}_2\text{O}_5]$ were performed in DACs using a custom-built set-up.¹⁶ For the generation of the fundamental pump wave we used an Impex HighTech Q-switched Nd:YAG laser (1064 nm, 5–6 ns, 2 kHz). The fundamental infrared light was separated from the generated second harmonic (532 nm) with a harmonic separator, a short-pass filter, and an interference filter. The SHG signal was collected using a photomultiplier tube (Hamamatsu R2949) in combination with an oscilloscope (Tektronix TDS2022). The sample was measured in transmission geometry using the Kurtz-Perry approach.¹⁷ Quartz (SiO_2) and corundum (Al_2O_3) powders outside a DAC at ambient conditions were employed as reference materials. For the samples in the DAC and the reference materials 40 individual SHG measurements were carried out and averaged, respectively. Background signals between the laser pulses were used to correct the measured SHG intensities using Matlab.

1.6. Density functional theory-based calculations

First-principles calculations were carried out within the framework of density functional theory (DFT), employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and the plane wave/pseudopotential approach implemented in the CASTEP simulation package.^{18–20} “On the fly” norm-conserving or ultrasoft pseudopotentials generated using the descriptors in the CASTEP data base were employed in conjunction with plane waves up to a kinetic energy cutoff of 1020 eV or 630 eV, for norm-conserving and ultrasoft pseudopotentials, respectively. The accuracy of the pseudopotentials is well established.²¹ A Monkhorst-Pack grid was used for Brillouin zone integrations.²² We used a distance between grid points of $<0.023 \text{ \AA}^{-1}$. Convergence criteria for geometry optimization included an energy change of $<5 \times 10^{-6} \text{ eV atom}^{-1}$ between steps, a maximal force of $<0.008 \text{ eV \AA}^{-1}$ and a maximal component of the stress tensor $<0.02 \text{ GPa}$. Phonon frequencies were obtained from density functional perturbation theory (DFPT) calculations.^{23,24} Raman intensities were computed using DFPT with the “ $2n + 1$ ” theorem approach.²⁵ The reliability of calculations of SHG tensors has been established previously.²⁶

2. Results

2.1. Single crystal synchrotron X-ray diffraction at 20 GPa

After their identification by Raman spectroscopy, we performed synchrotron X-ray diffraction in the region where mainly Raman modes of the unknown phase have been observed in the DAC. Fig. S 1 a shows a part of an *unwarped* image of the raw-experimental data after processing of the $(0kl)$ area in CrysAlis. Besides the reflection of the new phase, reflections and powder rings of different CO_2 phases, $\text{Na}_2[\text{CO}_3]$ and diamond are present. Projections of the reciprocal space show the distribution of reflections and the effect of the shading of diffracted beams due to the DAC in Fig. S 1 b after data reduction. Nevertheless, the coverage of the reciprocal space is sufficient for a subsequent single crystal structure solution.

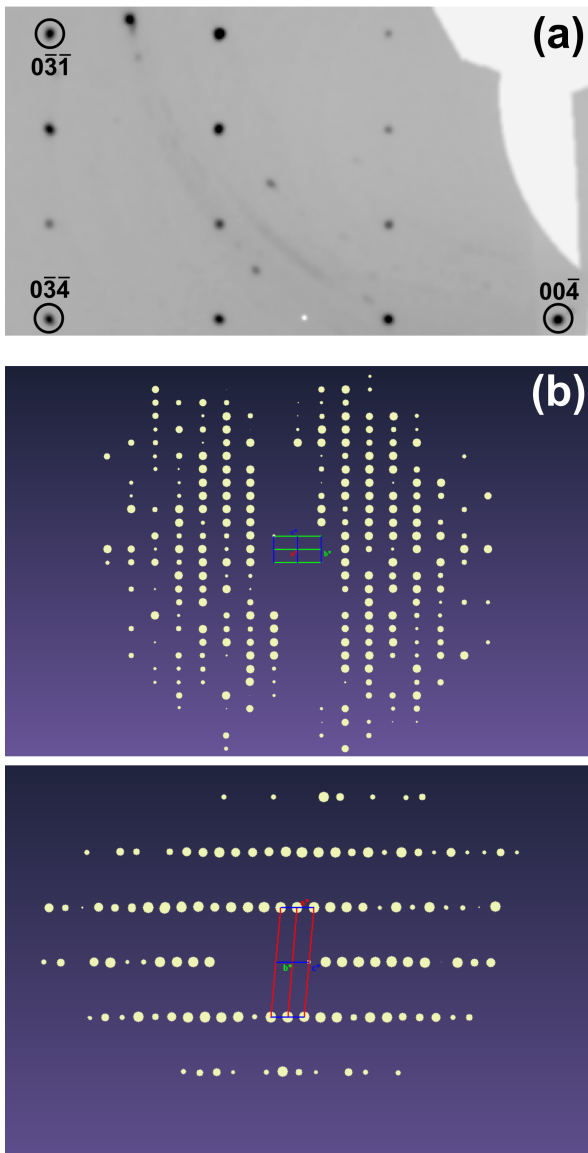


Figure S 1: (a) *Unwarped* image of the raw-experimental data after data reduction. The $(0kl)$ area is shown. Other reflections are due to other phases present in the sample chamber. (b) Schematic depiction of the reflections in reciprocal space using the Ewald-Explorer in CrysAlis after data reduction and later used for the refinement. Projections of the reciprocal space are shown along a^* (top) and b^* (bottom).

After the data reduction the crystal structure was solved in the monoclinic space group $P2_1$ (No. 4) with $Z = 2$. The new phase has $\text{Na}_2[\text{C}_2\text{O}_5]$ composition. The R -value (6.0%) and the reflection to parameter ratio (11:1) reveal a reasonable structure refinement. The displacement parameters of the sodium atoms were refined anisotropically. In order to reduce the amount of parameters the atomic displacement parameters of the carbon and oxygen atoms were refined isotropically. No constraints or restraints had been applied for the atomic positions or displacement parameters. The *PLATON*/checkCIF program does not suggest a higher space group symmetry or missing symmetry elements.²⁷ Table S 1 lists the crystallographic parameters of $\text{Na}_2[\text{C}_2\text{O}_5]$ valid for 20(2) GPa in comparison to DFT calculations.

Table S 1: Structural parameters of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 20(2) GPa from single crystal structure solution (ambient temperature) in comparison to theoretical data derived from DFT calculations (athermal limit).

	Single Crystal	DFT
Crystal data		
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Chemical formula	$\text{Na}_2[\text{C}_2\text{O}_5]$	$\text{Na}_2[\text{C}_2\text{O}_5]$
M_r	150.0	150.0
a (Å)	2.9064(8)	2.9694
b (Å)	5.4219(5)	5.4964
c (Å)	9.6871(9)	9.7458
α (°)	90.0	90.0
β (°)	94.99(1)	94.95
γ (°)	90.0	90.0
V (Å ³)	152.07(5)	158.47
Z	2	2
Data collection		
F_{000}	148	-
θ range (°)	1.76–16.53	-
measured reflections	714	-
independent reflections	710	-
reflections $I > 2\sigma(I)$	515	-
R_{int}	0.020	-
Refinement		
$R[F > 2\sigma(F)]$, $wR(F)$	0.060, 0.046	-
No. of reflections	515	-
No. of parameters	47	-
No. of restraints	0	-
No. of constraints	1	-
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.47, -0.52	-

The experimental and the theoretical structural model of $\text{Na}_2[\text{C}_2\text{O}_5]$ match within the expected errors. In addition, the DFT-based calculations confirmed the acentric, monoclinic space group symmetry of $\text{Na}_2[\text{C}_2\text{O}_5]$. The atomic coordinates and isotropic displacement are listed in Table S 2. Due to the presence of only light elements (sodium, oxygen and carbon) the intensity of the diffraction data is relatively low.

Table S 2: Atomic coordinates and isotropic displacement parameters of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 20(2) GPa obtained by single crystal structure refinement (1st line) or from DFT-based calculations (2nd line).

Atom	Site	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$
Na1*	2a	0.619(1)	0.4791(3)	0.8780(2)	0.013(1)
		0.62144	0.47657	0.87825	
Na2*	2a	0.525(1)	0.2117(3)	0.5831(2)	0.013(1)
		0.52711	0.21196	0.58269	
O1	2a	0.094(2)	0.7991(5)	0.8009(3)	0.0113(5)
		0.09351	0.80032	0.80137	
O2	2a	1.075(2)	0.2116(5)	0.7742(3)	0.0109(5)
		1.07410	0.20884	0.77345	
O3	2a	0.423(2)	0.5750(5)	0.6523(3)	0.0128(6)
		0.41925	0.57630	0.65346	
O4	2a	0.026(2)	0.8996(5)	0.5713(3)	0.0106(5)
		0.02999	0.89774	0.57192	
O5	2a	0.812(2)	0.0320(5)	0.9569(3)	0.0135(6)
		0.81231	0.03343	0.95629	
C1	2a	0.186(3)	0.7564(6)	0.6629(4)	0.0108(7)
		0.18336	0.75748	0.66411	
C2	2a	0.981(2)	0.0306(6)	0.8474(4)	0.0116(7)
		0.98635	0.03174	0.84563	

*anisotropic displacement parameters are listed in the cif-file

2.2. Second harmonic generation measurements at 5 GPa

To confirm the acentric space group symmetry, we performed measurements of the second harmonic generation. Therefore, the pressure in the DAC was decreased to 5(1) GPa, where no other CO_2 phase except CO_2 -I (dry ice) is present in the gasket hole. In addition, the Raman spectra measured during decompression show that $\text{Na}_2[\text{C}_2\text{O}_5]$ can be at least recovered down to 5(1) GPa. We measured an unambiguous SHG signal from the sample in the DAC (≈ 61 mV) confirming the acentric structural model for $\text{Na}_2[\text{C}_2\text{O}_5]$. The measurement was performed relative to the SHG intensities of quartz (acentric) and corundum (centrosymmetric) powders which were measured outside a DAC at ambient conditions as reference materials (Fig. S 2).

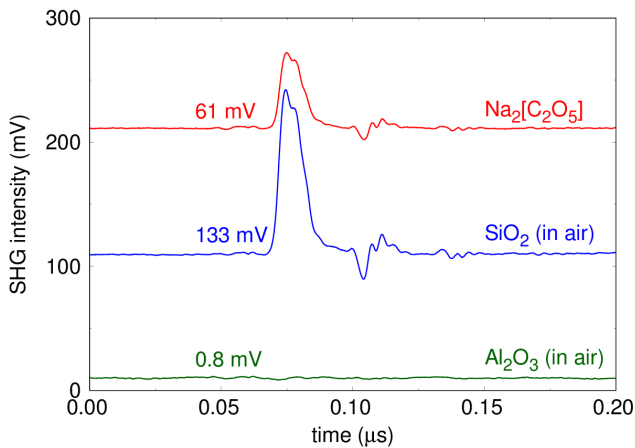


Figure S 2: SHG measurements of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 5(1) GPa in a DAC in comparison to the reference powders quartz (SiO_2) and corundum (Al_2O_3) measured outside a DAC at ambient conditions. The spectra of quartz and $\text{Na}_2[\text{C}_2\text{O}_5]$ are shown with an offset of 100 mV and 200 mV, respectively.

It is clear to see that no SHG signal can be observed from the centrosymmetric corundum powder (≈ 0.8 mV), while the acentric quartz sample shows a significant SHG signal (≈ 133 mV). Unfortunately, the actual SHG intensity from $\text{Na}_2[\text{C}_2\text{O}_5]$ cannot be quantified from these measurements, as the Kurtz-Perry approach does not result in absolute SHG intensities.¹⁷

2.3. DFT calculations on $\text{Na}_2[\text{C}_2\text{O}_5]$

In order to determine the SHG intensity of the $\text{Na}_2[\text{C}_2\text{O}_5]$ we used DFT-based calculations. As DFT-GGA-PBE calculations underestimate the band gap, the tensor components will be slightly overestimated.²⁶ We calculated the full SHG tensor of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 5 GPa:

$$d = \begin{pmatrix} 0.000 & 0.000 & 0.000 & 0.095 & 0.000 & -0.199 \\ -0.199 & -0.432 & 0.721 & 0.000 & 0.095 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.721 & 0.000 & 0.095 \end{pmatrix}$$

Furthermore, we used DFT-based calculations to obtain the pressure dependent p, V relation of $\text{Na}_2[\text{C}_2\text{O}_5]$. The calculations indicate that a pressure-induced phase transition may occur during decompression at ≈ 4.2 GPa as at this pressure a distorted polymorph becomes more stable in the athermal limit when entropic contributions are neglected. Both phase are closely related having monoclinic space group symmetry ($P2_1$ with $Z = 2$). Table S 3 shows the crystallographic data calculated for both phases at 5 GPa in comparison.

Table S 3: Structural parameters of the low- p and high- p phase of $\text{Na}_2[\text{C}_2\text{O}_5]$ obtained by DFT calculations (athermal limit) at 5 GPa.

	DFT (low- p phase)	DF (high- p phase)
Crystal data		
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Chemical formula	$\text{Na}_2[\text{C}_2\text{O}_5]$	$\text{Na}_2[\text{C}_2\text{O}_5]$
M_r	150.0	150.0
a (Å)	3.3127	3.2207
b (Å)	6.1611	5.7679
c (Å)	9.7267	10.1457
α (°)	90.0	90.0
β (°)	86.34	93.58
γ (°)	90.0	90.0
V (Å ³)	198.12	188.11
Z	2	2

The atomic coordinates of both phases at 5 GPa, obtained by from DFT-based calculations, are listed in Table S 4. The phase transition between both phases is discontinuous with a $\Delta V \approx 10 \text{ \AA}^3$ at 4.2 GPa.

Table S 4: Atomic coordinates of the low- p and high- p phase of $\text{Na}_2[\text{C}_2\text{O}_5]$ obtained by DFT calculations (athermal limit) at 5 GPa.

Atom	Site	x	y	z
high-p phase				
Na1	$2a$	0.61672	0.48130	0.87934
Na2	$2a$	0.51650	0.21841	0.58357
O1	$2a$	0.08156	0.80519	0.79760
O2	$2a$	1.04523	0.20061	0.77660
O3	$2a$	0.39032	0.58579	0.65589
O4	$2a$	0.04183	0.89647	0.57564
O5	$2a$	0.82253	0.01760	0.95409
C1	$2a$	0.17601	0.76266	0.66514
C2	$2a$	0.97394	0.02637	0.84460
low-p phase				
Na1	$2a$	0.74900	0.47493	0.88486
Na2	$2a$	0.31069	0.23727	0.57736
O1	$2a$	0.15976	0.86064	0.57498
O2	$2a$	0.76437	0.07297	0.95975
O3	$2a$	0.01096	0.83228	0.81008
O4	$2a$	0.77518	0.16177	0.73728
O5	$2a$	0.31346	0.56583	0.69711
C1	$2a$	0.17082	0.75103	0.68196
C2	$2a$	0.83675	0.03767	0.83430

The main difference between the high-pressure and the low-pressure polymorph is the tilt-angle in the $[\text{C}_2\text{O}_5]^{2-}$ -groups, which changes discontinuously at ≈ 4.2 GPa from $\approx 33^\circ$ in the high-pressure phase to $\approx 7^\circ$ in the low-pressure polymorph (Fig. S 3).

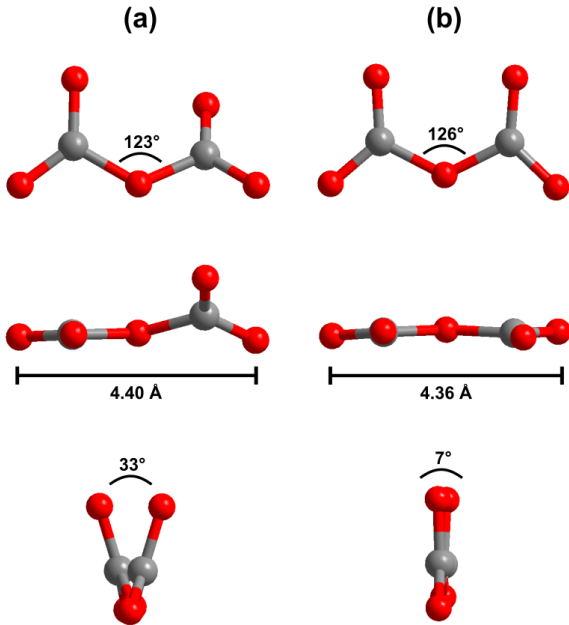


Figure S 3: Geometry of the $[\text{C}_2\text{O}_5]^{2-}$ -group in (a) the high- and (b) the low-pressure phase of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 5 GPa in comparison.

We used the p, V relation obtained from the DFT calculations to calculate the theoretical bulk modulus (K_0) for both phases. A 3rd-order Birch-Murnaghan equation of states (EOS) was fitted to unit cell volume obtained by the calculations between 0–10 GPa and 4–20 GPa, respectively (Fig. S 4).^{28,29} We used the software package EOSFit7-GUI.³⁰ The theoretical bulk modulus

of the high-pressure phase is $K_0 = 31.8(3)$ GPa with $K_p = 5.5(1)$ which is in the same range as observed for the other pyrocarboantes.^{3,31,32} The bulk modulus of the low-pressure phases is nearly identical ($K_0 = 32.0(6)$ GPa with $K_p = 4.1(1)$), but the pressure-dependence of the bulk modulus K_p is smaller.

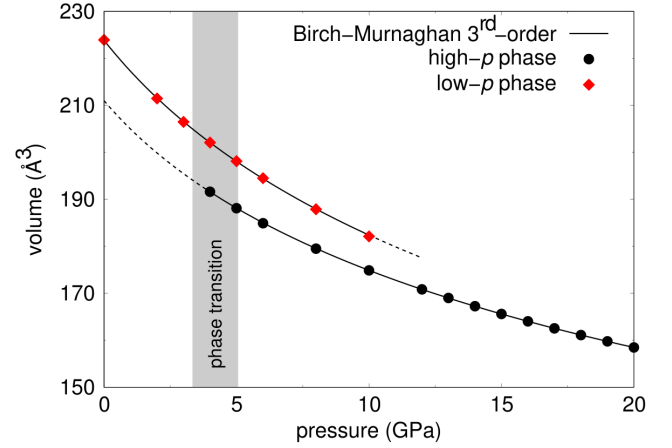


Figure S 4: Birch-Murnaghan EOS fitted to the unit cell volumes obtained by DFT-based calculations of the low- and the high-pressure phase of $\text{Na}_2[\text{C}_2\text{O}_5]$ between 0–10 GPa and 4–20 GPa, respectively. The DFT-calculations show a phase transition between both phases at ≈ 4.2 GPa.

We used the DFT calculations to obtain theoretical Raman spectra of the low- and the high-pressure phase of $\text{Na}_2[\text{C}_2\text{O}_5]$. Figure S 5 shows the calculated spectra for both phases at 5 GPa in comparison. There is a characteristic Raman mode at 846 cm^{-1} in the Raman spectra of the high-pressure phase, which will facilitate its identification in future experiments.

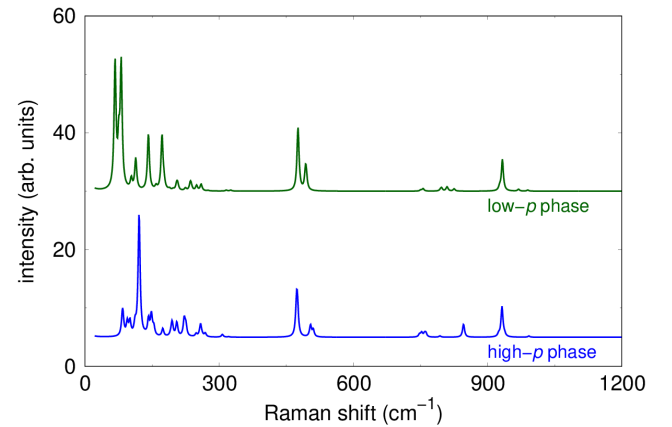


Figure S 5: Theoretical Raman spectra of the low-pressure and the high-pressure phase of $\text{Na}_2[\text{C}_2\text{O}_5]$ at 5 GPa obtained by DFT-based calculations. The shifts of the Raman spectra were rescaled by 4 %.

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