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The polymeric phase V of carbon dioxide has not been recovered at ambient pressure and has a unique structure

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In their high pressure study of solid CO₂, Yong et al (1) claim (i) that they recovered the polymeric phase V (CO₂-V) at ambient pressure and 191 K, and (ii) that CO₂-V may exist in different crystal structures. We demonstrate below that neither of these claims are supported by their data.

First, Yong et al show as evidence for the recovery of CO₂-V to ambient pressure a Raman spectrum of the sample labeled as "Ambient & 191 K" in Fig. 5B of Ref. (1). This spectrum does contain CO₂-V peaks at 360.8, 665.9, 880 and 978 cm⁻¹. It also displays two more peaks at 113.8 and 166.8 cm⁻¹ corresponding to the F_g⁻ and F_g⁺ librations of CO₂-I, respectively. This CO₂-V/CO₂-I coexistence originates from the kinetically-limited back-transformation of CO₂-V into CO₂-I which is the stable phase below 10 GPa. The two coexisting solids must be at the same pressure, and the latter may be determined from the well-documented frequencies of the Raman peaks of CO₂-I at ambient and high pressure (see Ref. (2) and references therein). Doing so shows that the "Ambient & 191 K" spectrum is not at ambient pressure* but at 1.9(1) GPa, a pressure similar to the lowest one at which CO₂-V has been observed at 300 K (1, 3–5). Therefore, CO₂-V has not been recovered at ambient pressure in Yong et al (1).

The second question is whether CO₂-V may have different structures depending on the sample thermodynamic history. Yong et al (1) argue this is why the x-ray diffraction (XRD) pattern measured by Ref. (3), on one hand, and by Refs. (4–6) on the other hand, are different, and propose a metastable structure of space group Pna2₁ to explain the XRD pattern of Ref. (3). Unlike what Ref. (1) states, the same structure of I-42d space group has been independently found in experiments by 3 different groups, whether phase V was obtained on heating phase II, III, IV or a mixture of these phases at various pressures from ~39 to ~75 GPa and therefore does not depend on the followed P-T path (4–6). The main difference between Refs. (4–6) and Ref. (3) is that the former directly heated pure CO₂ samples to obtain phase V, while the latter used indirect heating of CO₂ mixed with ruby to absorb the infrared laser. There are recent evidence that CO₂ reacts with other compounds at high P-T, including SiO₂ (7) and MgO (8, 9), suggesting that the XRD pattern of Ref. (3) is not from pure CO₂-V. Curiously, despite measuring different XRD patterns, Yoo et al (3) and Yong et al (1) obtained the same Raman spectra for phase V as Refs. (4–6). We compare in Fig.1 the theoretical spectra of I-42d and Pna2₁ structures to the experimental one of CO₂-V from Refs. (3, 4). Clearly the theoretical Raman spectra of I-42d is in good agreement with experiment, as previously found (4, 5), while that of Pna2₁ is largely different. There is thus no experimental evidence for the Pna2₁ structure.

* At ambient pressure and 191 K, F_g⁻ and F_g⁺ are, respectively, at 81(1) cm⁻¹ and 117(2) cm⁻¹, that is, respectively 33 cm⁻¹ and 50 cm⁻¹ below the observed peaks.

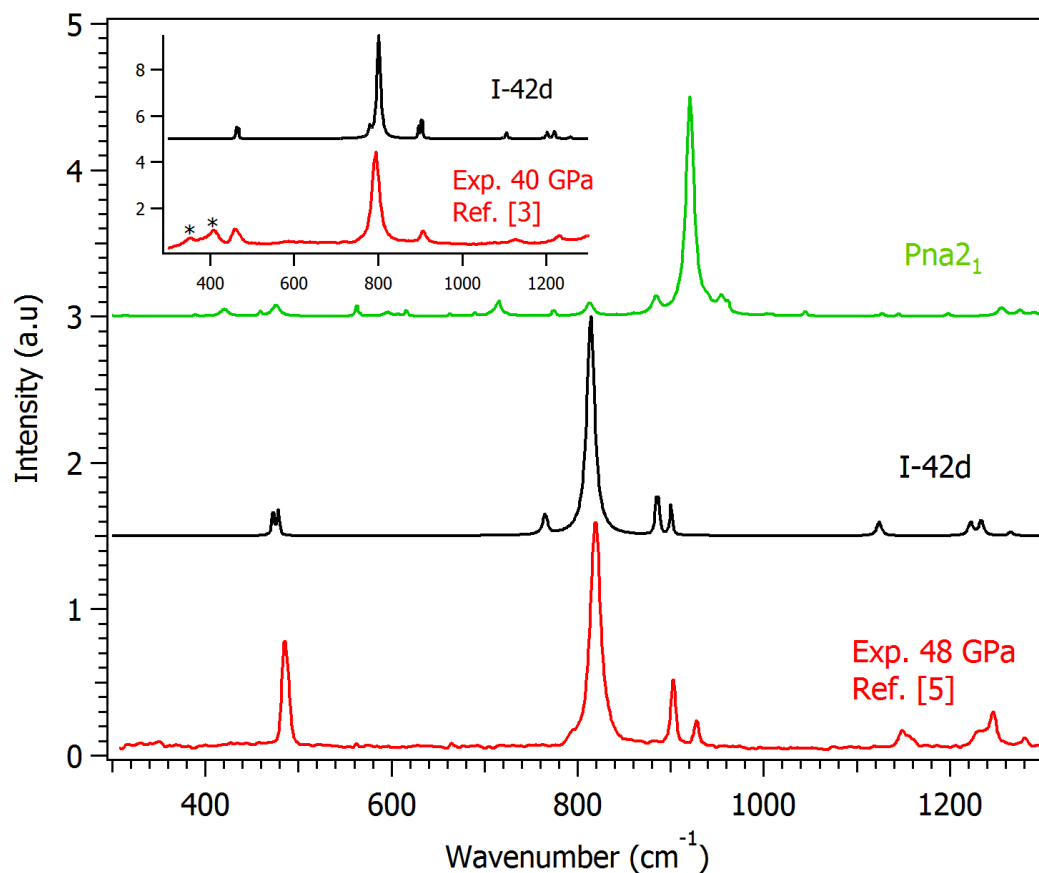


Fig. 1: Raman spectrum of CO₂-V. The main window shows the experimental spectrum (bottom, red line) at 48 GPa, 300 K from Ref. (4), and the theoretical ones for the I-42d structure (4, 5) (middle, black line) and the Pna2₁ structure (1) (top, green line) at 50 GPa, 0 K. The subset window shows the experimental spectrum at 40 GPa, 300 K from Ref. (3) and the theoretical one for the I-42d structure (4, 5) at 40 GPa, 0 K. The asterisks indicate Raman peaks from the untransformed molecular CO₂ in the experimental spectrum of Ref. (3). The theoretical spectra were obtained by state-of-the-art ab initio calculations based on Density Functional Perturbation Theory, as implemented in the Quantum-Espresso code (10). Lorentzian profiles with arbitrary linewidths have been used for the theoretical spectra.

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