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Electronic Supplementary Information for:

Germanium-73 NMR of Amorphous and Crystalline GeO_2

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Experimental

Sample Preparation:

Samples were prepared from 99.999% purity quartz-phase GeO_2 (Matheson Coleman & Bell), without further purification. Rutile-phase GeO_2 was prepared by grinding the quartz phase with 0.5 mol% Li_2GeO_3 in a small amount of acetone, and heating the resultant mixture (after evaporation of residual acetone) in a Pt/Au crucible at 900 ^oC for 30 hours.[i,ii] The product was allowed to cool, was reground, and heated again at 900 ^oC for another 24 hours to improve crystallinity. The structures of both crystalline phases were confirmed by x-ray diffraction. Vitreous GeO_2 was prepared by heating GeO_2 (quartz-like) in a Pt/Au ZGS crucible at 1400 ^oC for three hours before quenching the melt in a water bath. The product was examined under a polarized light microscope at 50x magnification and found to be homogenous with no visible crystalline impurities.

Nuclear Magnetic Resonance Spectroscopy:

Germanium-73 NMR spectra of all samples were collected on a Bruker Avance II 900 MHz (B_o = 21.1 T) spectrometer at the National Ultrahigh Field NMR Facility for Solids using a single-channel 7 mm MAS probe (Bruker). Solid-echo (90^o-τ-90^o) spectra of non-spinning samples used a 2 μs solid 90^o pulse (ν_{rf} = 25 kHz), 10 992 to 28 000 scans and a recycle delay of

2 to 5 seconds. Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG)[iii] experiments were done with 2 μs 90° pulses, 4 μs 180° pulses. 32 to 256 echoes were collected, as permitted by the T_2 of the sample. QCPMG-MAS spectra at a spinning frequency of 8 kHz were acquired for both the quartz-like phase and the vitreous GeO_2 sample at 21.1T using the same probe and similar parameters to the non-spinning QCPMG. Due to the breadth of the signals, all spectra were collected in a piecewise manner (512 to 2056 co-added transients per piece) by shifting the transmitter frequency by 16,000 to 27,000 Hz, and summed to provide the complete spectrum. The number of pieces varied from three to eight depending upon the breadth of the NMR signal. The quartz phase was found to yield identical spectra whether collected as one or three pieces due to sufficiently short excitation pulses and a narrower central transition than the rutile-like and vitreous GeO_2 samples.

^{73}Ge spectra of the quartz-like phase were also acquired on a Bruker AMX 500 (B_o = 11.74 T) operating at 17.43 MHz using either a 10 mm saddle-coil ("liquids") probe or a home-built 5 mm low-gamma probe equipped with an 10-turn solenoidal coil oriented orthogonally to the direction of the static field. Both a Hahn-echo sequence (90°-τ-180°) employing the extended phase-cycling scheme of Oldfield[iv] as well as QCPMG[iii] were used. For the former, 20,000 scans were collected with a recycle delay of 5 s and using a 10 μs 90° pulse. For the latter sequence a total of 512 echoes were collected with a recycle delay of 5 s and 44,341 co-added transients. Power levels were set to yield a 2.2 μs 90° pulse.

All spectra were referenced with respect to tetramethylgermanium, using the secondary reference, $GeCl_4$ at 30.9 ppm.

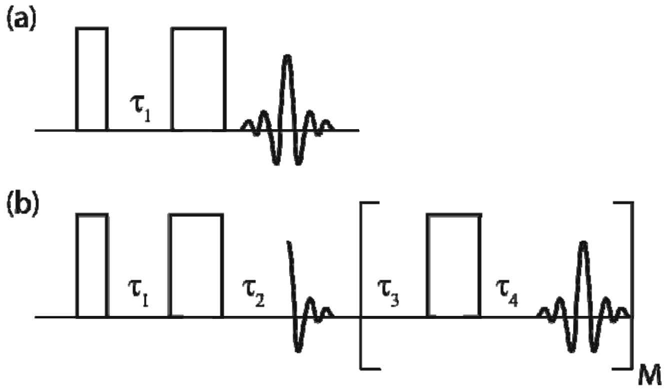

Figure S1: a) spin-echo pulse sequence; b) QCPMG pulse sequence

***Calculations*:**

Density functional theory (DFT) calculations were done with the NMR package in CASTEP version 4.3[v] to obtain electric field gradients (EFGs) and electronic shielding at germanium in both crystalline GeO_2 phases. The EFG calculations used a plane-wave basis set cutoff energy of 610 eV and the PBE functional. Although CASTEP uses -0.173 barn to determine the quadrupolar coupling tensors of Ge, we have recalculated them with the more commonly used value of -0.196 barn.[vi]

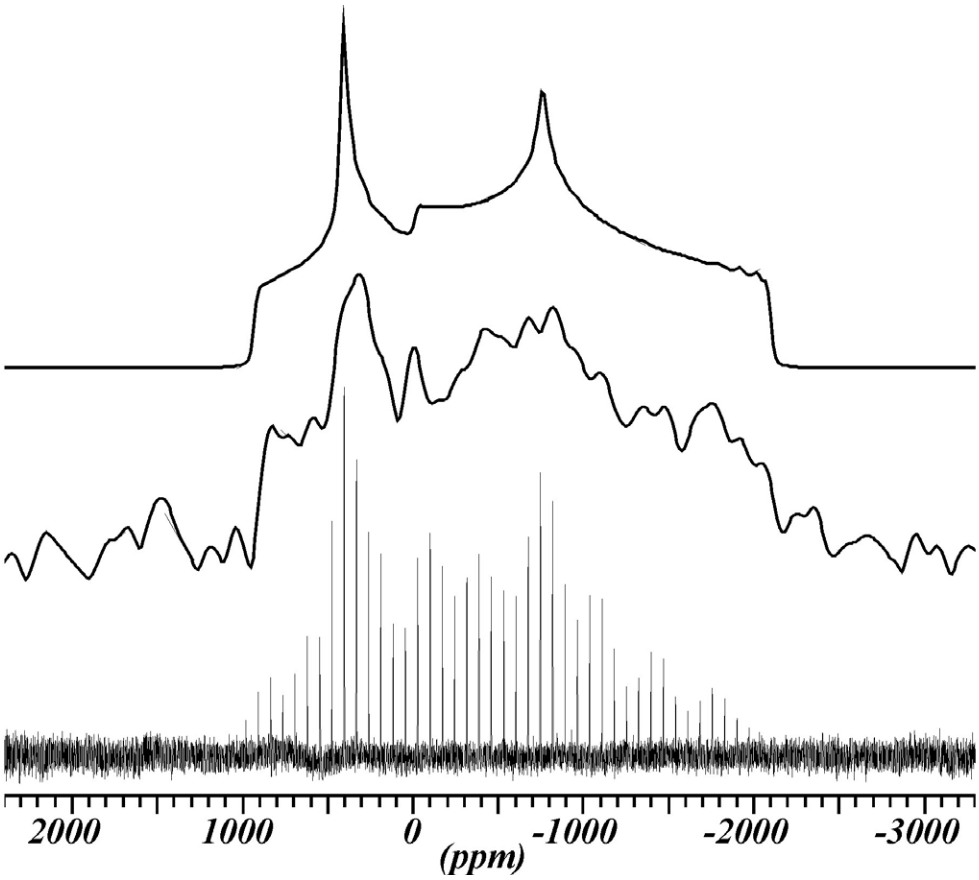

Figure S2: Quartz-like GeO_2 acquired at 500 MHz. Simulation (top), solid-echo (middle) and QCPMG (bottom).

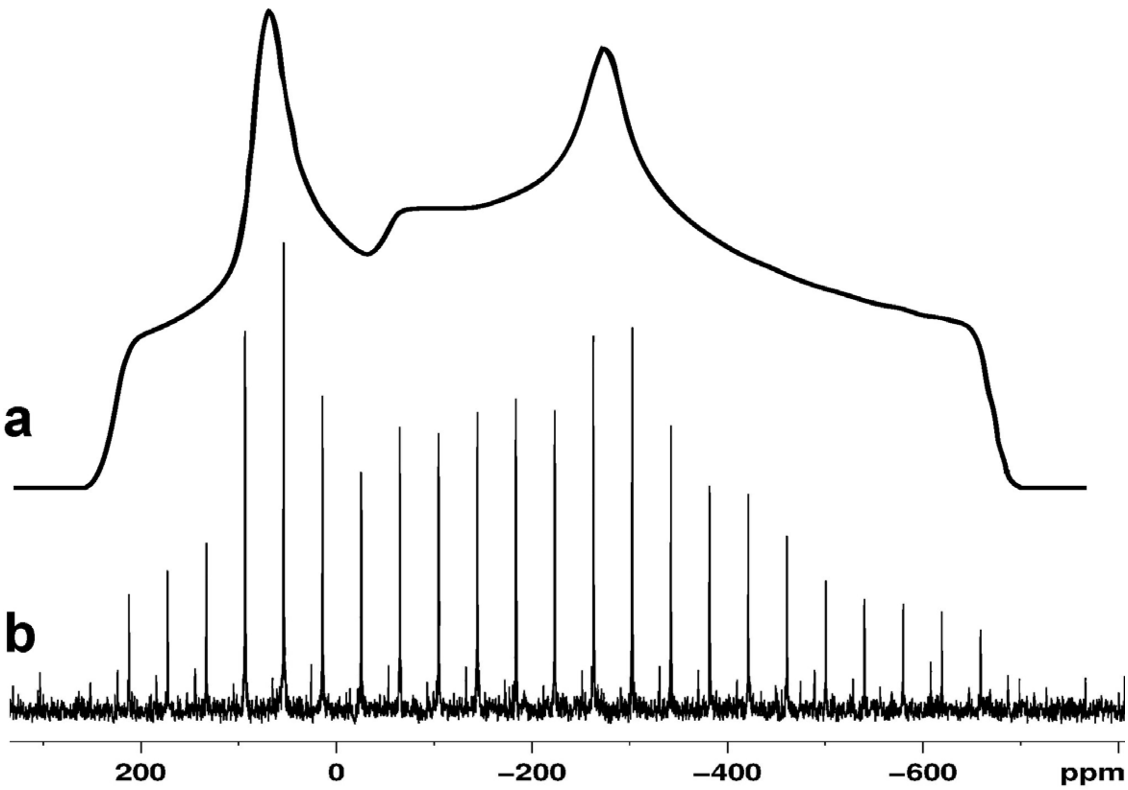

Figure S3: Quartz-like GeO_2 acquired at 900 MHz. Simulation (a) and QCPMG (b).

References

i) Hussin, R.; Holland, D.; Dupree, R., *Journal of Non-Crystalline Solids* 1998, *234*, 440
ii) Du, L.S.; Stebbins, J.F., *Journal of Physical Chemistry B* 2006, *110*, 12427
iii) Larsen, F. H.; Jakobsen, H. J.; Ellis, P. D.; Nielsen, N. C. *Journal of Physical Chemistry A* 1997, *101*, 8597.
iv) Kunwar, A. C.; Turner, G. L.; Oldfield, E. *Journal of Magnetic Resonance* 1986, *69*, 124.
v) Profeta, M. M., Mauri, F., Pickard, C.J. *Journal of the American Chemical Society* 2003, *125*, 541.
vi) Harris, R.; Becker, E. *Journal of Magnetic Resonance* 2002, *156*, 323