Electronic Supplementary Information (ESI) for

Pauling's third rule beyond the bulk: chemical bonding at quartz-type GeO_2 surfaces

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Convergence Tests. To make sure that relevant computational parameters suffice, we performed a number of convergence tests. The results for surface energies γ are shown in *Figure S1*. First, we have plotted the computed γ for the (001) surface as obtained with increasingly thick slabs (Figure S1a). While a slab of approximately 17 Å thickness already provides satisfactory results in accord with a previous study on silica (001) (Ref. 25 in the Article), we opt for a slightly thicker one, containing 12 formula units (36 atoms). The surface unit cells for the other models are larger, and so the corresponding slab cells contain a larger number of 13–17 formula units.

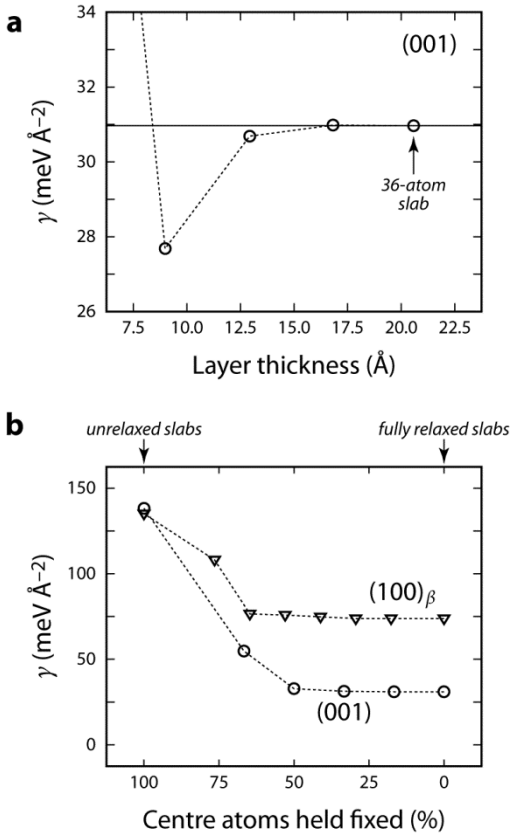

Figure S1: Surface energies γ computed for selected q-GeO_2 surfaces during convergence tests. Therein, either the layer thickness was varied (a), or a number of atoms was held fixed in the center, "bulklike" region of the slab models (b).

In *Figure S1b*, we show the computed surface energy upon holding a certain number of atoms fixed in the interior of the slab, as we have done in a recent study of layered germanium–antimony tellurides (Ref. 41 in the Article). Zero relaxed atoms correspond to the freshly cleaved (unrelaxed) slab; upon releasing more and more atoms, the predicted surface energy γ is noticeably lowered but—and this is, in our opinion, important to ensure sufficient size of the slabs—whether a few atoms held fixed in the centre (< 50%) or not (0%) does not affect the computed surface energies in a noticeable way.

It is also mandatory to check the convergence of computed pCOOP curves with regard to reciprocal-space (**k** point) sampling. Structures have been relaxed using rather large grids which are well-manageable for this purpose in terms of computational time. pCOOP analysis, on the other hand, requires the output of "wavefunctions" (plane-wave coefficients, which in a default VASP relaxation run do not need to be stored) which are then read and processed by the projection software; this places high demands on disk space and memory. We illustrate this at the hand of an example: the (100)β surface, for which results are shown in Figure 11 of the Article. A computation on the full grid of 117 **k** points gave a wavefunction file of 6.0 GB file size, and the pCOOP analysis required a time of slightly over 14 hours. Reduction to 20 **k** points gave a wavefunction file of 1.1 GB, and the pCOOP computation was completed within 2 hours and 20 minutes. In Figure S2, the results obtained in both cases are contrasted: clearly, there is no difference in interpretation but only extremely slight numerical fluctuations. We conjecture that similar, reduced **k** point grids give properly converged pCOOP data also for the other surfaces.

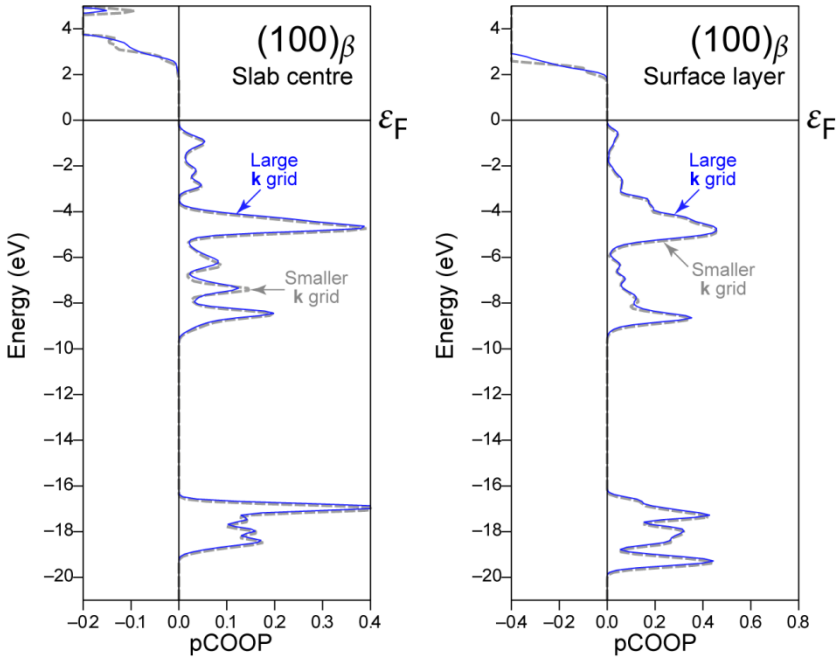

Figure S2: Output of pCOOP computations (see Ref. 49 in the Article), plotted using the wxDragon software.[S1] Data obtained on a smaller **k** point grid (20 points, also shown in Figure 11 of the Article) are plotted here with dashed grey lines; they are overlaid by data obtained on large **k** point grids of 117 points (solid blue lines). Note that in the case of the surface layers, the pCOOP values are shown as raw output over two tetrahedra (centred at atoms 44 and 50), that is, eight Ge–O bonds. For the presentation in the Article, they have been re-normalised to *one* tetrahedron (i.e., the pCOOP values on the horizontal axis are divided by two), as stated there.

We also computed bond populations (integrated pCOOPs) for the curves shown in Figure S2, and found that in either case, the results with "large" and "smaller" **k** point grids deviated by no more than ±0.001, respectively. This justifies to use the much more efficient, "small" **k** point grids with confidence.

Validation Studies for the Projection Technique. Here we provide additional validation regarding the suitability of the "projected COOP" bonding analysis. As reference, we show data obtained from tight-binding LMTO computations in the atomic-spheres approximation (TB-LMTO-ASA program, version 4.7)[S2–S4] on a tight **k** point mesh of 26×26×18 points; these computations constitute the reference to which the plane-wave based approach must stand up. First, we look at the atom-resolved densities of states (DOS) in *Figure S3* where we show contributions of Ge atoms (black lines) and O atoms (red lines) separately. The overall resemblance, especially with regard to relative band fillings, between both methods is clearly satisfactory.

Figure S3 also outlines the effect of the different approaches to reciprocal-space integration, both of which may be used for projected bonding analysis in the bulk: either the tetrahedron method[S5,S6] or broadening with a Gaussian function. They change the shape of the curves, but not their character or chemical interpretation. For all computations shown in the Article, a Gaussian broadening scheme is employed using reduced **k** point grids as discussed above (Figure S2).

Figure S4, finally, contrasts TB-LMTO-ASA computed crystal orbital Hamilton populations[S7] with the results of the pCOOP approach. Note that the absolute values (horizontal axis) must not be directly compared; one refers to energy partitioning, one to that of the electronic density. Nonetheless, the qualitative information (the shape of the curves, which reflects the chemical-bonding nature) is well described by either approach.

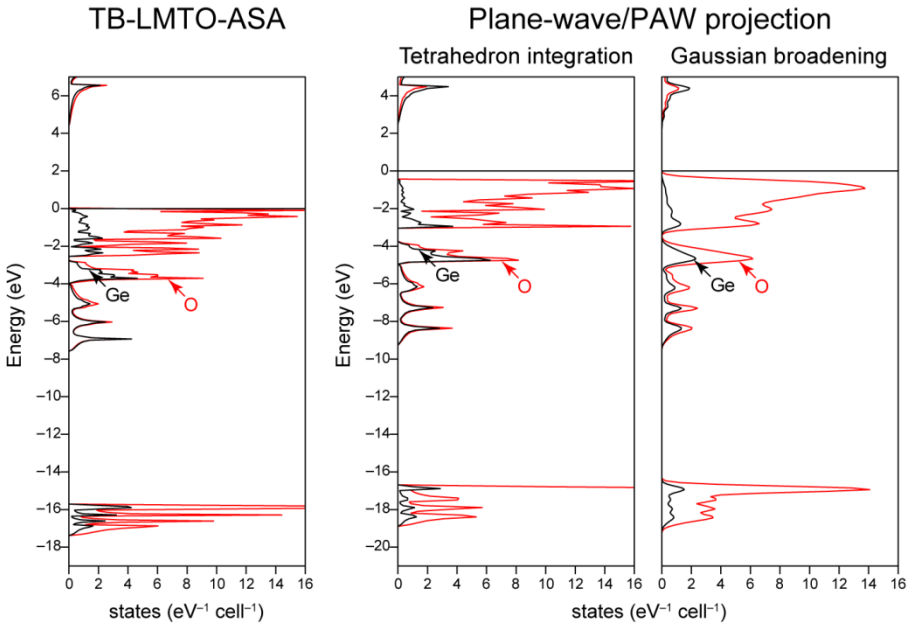

Figure S3: Electronic densities of states (DOS) for bulk quartz-type GeO_2 as computed with the reference code TB-LMTO-ASA (*left*), and projected DOS based on plane-wave DFT as used in the present study. Data are shown as obtained from tetrahedron integration (*middle*) and Gaussian smearing (*right*) routines; the latter is mandatory when moving from the bulk to surfaces. The band width and band gap is slightly different between the LMTO and plane-wave approaches, not surprisingly so because of the different basis sets and exchange–correlation functionals used. Hence, the energy scales are shifted such as to make visual comparison easy. The Fermi level ε_F is set to zero in all cases.

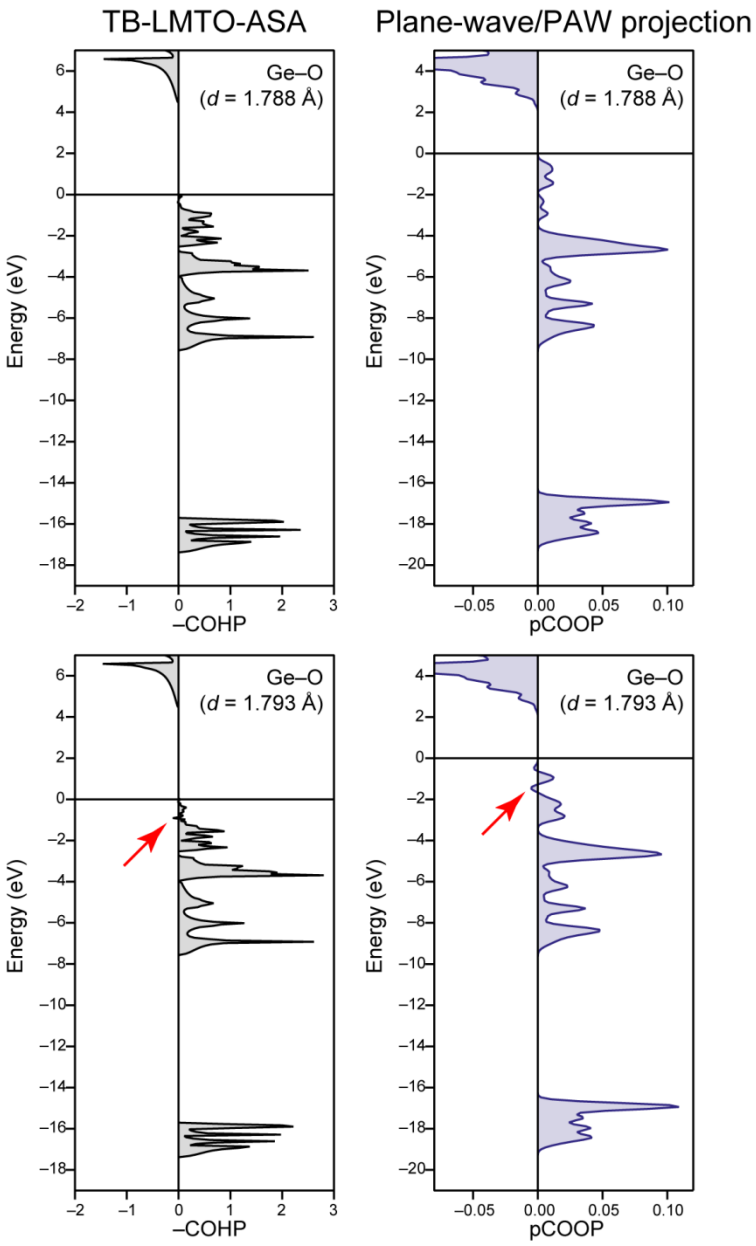

Figure S4: Computed crystal orbital Hamilton population (–COHP) and projected crystal orbital overlap population (pCOOP) curves for the two slightly different bonds in q-GeO_2. Note the slightly different characters of the two bonds of different length, especially visible in the vicinity of the Fermi level, which is captured in qualitatively comparable ways through both approaches (highlighted with an arrow for the longer bond).

Molecular-Dynamics Results for (001) and (100) Surfaces.

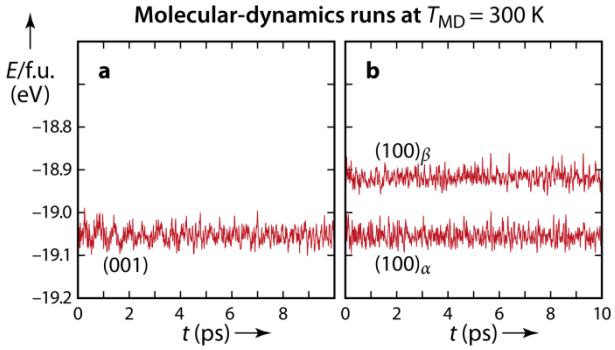

Figure S5: As Figure 6 in the Article, but for (001) and the two (100) surfaces. In all these cases, no changes in energy are seen except for normal fluctuations.

Role of the Subsurface Fragment at the (100)β surface. Here, we supplement Figure 11 in the Article in which, for the latter surface, an apparent "outlier" was found in the plot of bond populations vs. surface distance. That data point was labelled "subsurface fragment" in Figure 11, and *Figure S6* provides a detailed picture of the corresponding structural motif. It makes clear that this subsurface [GeO_4] entity is strongly strained, as well; this, again, is reflected in the computed pCOOP curve which is shown on the right of *Figure S3*. In particular, the bonding Ge–O interaction at ≈ 5 eV below the Fermi level is noticeably weakened in the subsurface fragment (bold orange line), as compared to the bulklike slab centre (dashed black line). In conclusion, the data point in Figure 11 should not be seen as an "outlier"; its role can be clearly correlated with the subsurface structure. *Together*, the surface and subsurface [GeO_4] motifs destabilise the "β" termination.

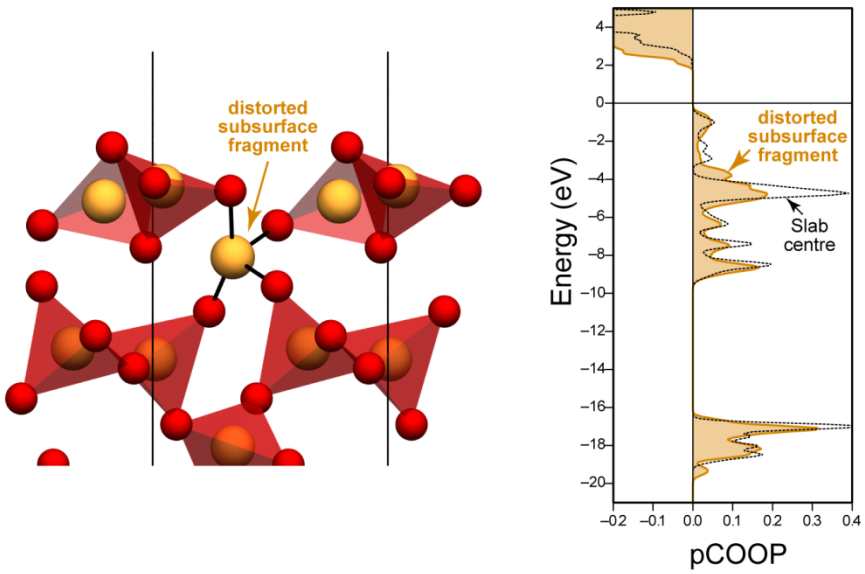

Figure S6: *Left:* Structural drawing of the subsurface [GeO_4] entity below the optimized (100)β surface; tetrahedra surrounding it have been sketched in polyhedral representation. *Right:* pCOOP analysis for the highlighted [GeO_4] motif (orange) and one in the slab center (as in *Figure S2*, dashed black line).

Structural Data. In the following, we provide structural data for the simulation cells used.

Table S1: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (001) surface. Lattice parameters: $a = b = 5.0983$ Å; c = 34.8844 Å. $\alpha = \beta = 90°$; $\gamma = 120°$.

O	0.14931576	0.63800503	0.82013019
O	0.83881898	0.98401860	0.81828299
O	0.49758039	0.28644978	0.82376892
O	0.17403155	0.99021768	0.75184768
O	0.82492620	0.33666833	0.75063444
O	0.55116679	0.77599863	0.71006636
O	0.43435014	0.21686471	0.67802862
O	0.09031939	0.50114881	0.65043027
O	0.71059680	0.74181023	0.62718430
O	0.30098281	0.02758424	0.59597202
O	0.90106053	0.42792965	0.56930748
O	0.60091031	0.81892522	0.54011012
O	0.38700132	0.21238004	0.51406794
O	0.08832864	0.52222950	0.48456671
O	0.68938483	0.72450909	0.45831058
O	0.28045872	0.03216413	0.42726250
O	0.89964112	0.41350627	0.40334948
O	0.55405090	0.78489162	0.37603707
O	0.43489908	0.22625346	0.34417389
O	0.16234229	0.51345050	0.30347165
O	0.81297994	0.81730582	0.30220758
O	0.48947913	0.79087240	0.23031897
O	0.14826642	0.14715508	0.23580340
O	0.83807709	0.49074385	0.23389550
Ge	0.16781592	0.97720242	0.80330710
Ge	0.82629309	0.30985034	0.80226866
Ge	0.49846982	0.08709520	0.72269534
Ge	0.45196732	0.56689399	0.66619593
Ge	-0.00095140	0.66581392	0.61085480
Ge	0.54136765	0.12122392	0.55479902
Ge	0.44736474	0.57444580	0.49928724
Ge	0.99212580	0.66649527	0.44329149
Ge	0.53688540	0.11739622	0.38791788
Ge	0.48876063	0.59036057	0.33142114
Ge	0.16083050	0.48550409	0.25183120
Ge	0.81925460	0.81121220	0.25074432

Table S2: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (100)α surface. Lattice parameters: *a* = 44.1526 Å; *b* = 5.0983 Å; c = 5.8141 Å. α = β = γ = 90°.

O	0.30750172	0.83116075	0.91130347
O	0.51012301	0.89937759	0.90811302
O	0.69231447	0.72851884	0.91965479
O	0.40891253	0.39533000	0.90325523
O	0.60454067	0.35203659	0.93060625
O	0.66340116	0.19871292	0.75221115
O	0.36460369	0.71947824	0.72846126
O	0.57236961	0.80341806	0.76576181
O	0.46971448	0.30961296	0.75319970
O	0.63539631	0.71947824	0.60487274
O	0.33659884	0.19871292	0.58112285
O	0.53028552	0.30961296	0.58013430
O	0.42763039	0.80341806	0.56757219
O	0.30768553	0.72851884	0.41367821
O	0.39545933	0.35203659	0.40272675
O	0.59108747	0.39533000	0.43007777
O	0.48987699	0.89937759	0.42521998
O	0.69249828	0.83116075	0.42202953
O	0.56023350	0.94740050	0.25020391
O	0.36412375	0.88848014	0.21421236
O	0.66055967	0.37984306	0.23065674
O	0.46050743	0.44946470	0.24094895
O	0.33944033	0.37984306	0.10267626
O	0.63587625	0.88848014	0.11912064
O	0.43976650	0.94740050	0.08312909
O	0.53949257	0.44946470	0.09238405
Ge	0.60073988	0.56879022	0.68694022
Ge	0.39926012	0.56879022	0.64639311
Ge	0.32882737	0.86243094	0.65086982
Ge	0.50000000	0.09926141	0.66666667
Ge	0.67117263	0.86243094	0.68246351
Ge	0.35981555	0.21457830	0.32485275
Ge	0.45388556	0.77980780	0.33159570
Ge	0.67075618	0.71336643	0.18370087
Ge	0.55487887	0.28070377	0.33602818
Ge	0.54611444	0.77980780	0.00173730
Ge	0.44512113	0.28070377	0.99730482
Ge	0.32924382	0.71336643	0.14963213
Ge	0.64018445	0.21457830	0.00848025

Table S3: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (100)β surface. Lattice parameters: *a* = 44.1526 Å; *b* = 5.0983 Å; c = 5.8141 Å. α = β = γ = 90°.

O	0.30900869	0.81830129	0.86170325
O	0.50944445	0.81247351	0.91142310
O	0.71284115	0.96907829	0.02967881
O	0.40881502	0.31402426	0.91055854
O	0.61372663	0.33380908	0.89917379
O	0.67697612	0.26963608	0.75965809
O	0.37175579	0.75389374	0.77504106
O	0.74449161	0.86833526	0.66998808
O	0.57005581	0.72258093	0.75604424
O	0.27482203	0.30709598	0.86392821
O	0.46982582	0.22158068	0.75581076
O	0.62824421	0.75389374	0.55829294
O	0.32302388	0.26963608	0.57367591
O	0.53017418	0.22158068	0.57752324
O	0.72517797	0.30709598	0.46940579
O	0.25550839	0.86833526	0.66334592
O	0.42994419	0.72258093	0.57728976
O	0.28715885	0.96907829	0.30365419
O	0.38627337	0.33380908	0.43415921
O	0.59118498	0.31402426	0.42277446
O	0.49055555	0.81247351	0.42190990
O	0.69099131	0.81830129	0.47162975
O	0.56080511	0.85954323	0.24602220
O	0.76882392	0.94183282	0.17307388
O	0.35485316	0.89207234	0.25308472
O	0.66324501	0.39570462	0.24277000
O	0.45970761	0.35857452	0.24577969
O	0.25117677	0.42088702	0.34076792
O	0.33675499	0.39570462	0.09056300
O	0.64514684	0.89207234	0.08024828
O	0.43919489	0.85954323	0.08731080
O	0.23117608	0.94183282	0.16025912
O	0.54029239	0.35857452	0.08755331
Ge	0.74882323	0.42088702	0.99256508
Ge	0.60086649	0.52381279	0.65901135
Ge	0.39913351	0.52381279	0.67432199
Ge	0.29251782	0.05782490	0.67337951
Ge	0.50000000	0.01054241	0.66666667
Ge	0.70748218	0.05782490	0.65995383
Ge	0.34973275	0.22520247	0.34222166

Ge	0.25290421	0.76276467	0.37426910
Ge	0.45435335	0.69175132	0.33287478
Ge	0.65639494	0.72541348	0.33871921
Ge	0.73865352	0.18457902	0.20770140
Ge	0.55504586	0.19179898	0.33520091
Ge	0.54564665	0.69175132	0.00045822
Ge	0.26134648	0.18457902	0.12563160
Ge	0.44495414	0.19179898	0.99813209
Ge	0.34360506	0.72541348	0.99461379
Ge	0.74709579	0.76276467	0.95906390
Ge	0.65026725	0.22520247	0.99111134

Table S4: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (101) surface. Lattice parameters: *a* = 5.0983 Å; *b* = 40.0000 Å; c = 7.7328 Å. α = β = 90°; γ = 109.248°.

O	0.99727853	0.36022454	0.93835513
O	0.51969896	0.32665841	0.98431829
O	0.06297008	0.28981202	0.03736397
O	0.70144384	0.42177397	0.90780392
O	0.17664275	0.46788749	0.85703901
O	0.12584840	0.63087278	0.81646162
O	0.54457395	0.58761985	0.80700031
O	0.02963296	0.55648324	0.77336123
O	0.57805061	0.51435649	0.81350518
O	0.64658501	0.66926368	0.68649206
O	0.65085046	0.30154979	0.69618587
O	0.45560630	0.45660517	0.56901639
O	0.94573840	0.41445068	0.60816365
O	0.42718627	0.38328541	0.57592074
O	0.99944338	0.34000428	0.56592104
O	0.01025965	0.50287102	0.52616428
O	0.48453945	0.54918954	0.47454326
O	0.71835775	0.68109481	0.34554723
O	0.22773468	0.64420024	0.39816988
O	0.75095161	0.61066392	0.44362979
O	0.66544766	0.28338109	0.32231535
O	0.38670967	0.33736001	0.32378331
O	0.86191424	0.38438843	0.25512246
O	0.80103878	0.54789645	0.22258563
O	0.20065302	0.49981274	0.19862086
O	0.69372528	0.47093049	0.18467661
O	0.26916358	0.42290171	0.16066716

O	0.29880028	0.58640842	0.12688542
O	0.75506898	0.63353687	0.05885523
O	0.03596290	0.68744608	0.06035093
Ge	0.88651442	0.65414114	0.89296999
Ge	0.25544735	0.58999556	0.88866359
Ge	0.81372652	0.32072485	0.91439756
Ge	0.66300939	0.55164704	0.71684219
Ge	0.31064723	0.48545347	0.69153408
Ge	0.63627136	0.41924986	0.66538022
Ge	0.59164893	0.65015336	0.46816652
Ge	0.05643045	0.38088102	0.49346441
Ge	0.68378286	0.31670688	0.48965627
Ge	0.94152051	0.66380551	0.23289280
Ge	0.59095291	0.57379359	0.31515366
Ge	0.91640059	0.50557905	0.28221520
Ge	0.32587078	0.46519207	0.10103783
Ge	0.96631564	0.39707019	0.06717610
Ge	0.39892964	0.30707282	0.14974777

Table S5a: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (011) surface, *after the initial conjugate-gradient relaxation* (no molecular-dynamics run). Lattice parameters: *a* = 5.0983 Å; *b* = 7.7328 Å; c = 30.0000 Å. $\alpha = \beta = 90°$; $\gamma = 109.248°$.

O	0.12793517	0.74890414	0.86425858
O	0.59076126	0.43715971	0.84155827
O	0.04151870	0.18715301	0.82167307
O	0.46405518	0.04558071	0.80330582
O	0.74053543	0.77478616	0.78923687
O	0.00356442	0.52641735	0.77552459
O	0.42257474	0.32584889	0.74708030
O	0.86361629	0.05600021	0.72813609
O	0.30100926	0.82809526	0.71261442
O	0.72901471	0.65918812	0.69453989
O	0.04079814	0.43161776	0.68555681
O	0.29779901	0.17191162	0.65911149
O	0.70030461	0.95420988	0.63701609
O	0.17874543	0.69774692	0.61084357
O	0.60958937	0.47145417	0.59742937
O	0.02402220	0.30031783	0.58396263
O	0.36688451	0.07402508	0.57054843
O	0.63198073	0.81756212	0.54437591

O	0.01177239	0.59985938	0.52228051
O	0.49506638	0.34015424	0.49583519
O	0.95571260	0.11258388	0.48685211
O	0.35880000	0.94367574	0.46877758
O	0.69350108	0.71577079	0.45325591
O	0.98261185	0.44592311	0.43431170
O	0.36303306	0.24535465	0.40586741
O	0.85163526	0.99698584	0.39215513
O	0.30436048	0.72619129	0.37808618
O	0.74025169	0.58461899	0.35971893
O	0.03948755	0.33461229	0.33983373
O	0.26491704	0.02286786	0.31713342
Ge	0.78130217	0.00641674	0.79530225
Ge	0.89762055	0.63209462	0.82595278
Ge	0.40225490	0.26161335	0.80581492
Ge	0.01675013	0.61533093	0.72122759
Ge	0.16179028	0.25570162	0.70602826
Ge	0.64161498	0.86231101	0.69241189
Ge	0.33031345	0.25913300	0.60300613
Ge	0.46467780	0.88588600	0.59069600
Ge	0.95706644	0.51263900	0.57838587
Ge	0.66518997	0.90946099	0.48898011
Ge	0.79197566	0.51607038	0.47536374
Ge	0.28730520	0.15644007	0.46016441
Ge	0.02652755	0.51015865	0.37557708
Ge	0.15141192	0.13967638	0.35543922
Ge	0.66077243	0.76535626	0.38608975

Table S5b: Fractional atomic coordinates for the fully relaxed simulation cell used to represent the q-GeO_2 (011) surface, *after the molecular-dynamics run*. Lattice parameters: a = 5.0983 Å; b = 7.7328 Å; c = 30.0000 Å. $\alpha = \beta = 90°$; $\gamma = 109.248°$.

O	0.83965921	0.81765722	0.86163251
O	0.54821836	0.44022064	0.84290711
O	0.00169929	0.19410166	0.82184466
O	0.43363190	0.04055816	0.83540352
O	0.64084185	0.79656211	0.78294039
O	0.03309034	0.59727097	0.78441200
O	0.44988109	0.28864290	0.75523147
O	0.91313372	0.06112181	0.72504908
O	0.33374691	0.84341634	0.70878485

O	0.75419683	0.65828452	0.70092797
O	0.10596833	0.44383225	0.69676775
O	0.39920083	0.20852914	0.66285554
O	0.75005311	0.94051746	0.63698991
O	0.22151794	0.69642378	0.60812389
O	0.65366028	0.47361855	0.59084477
O	0.06542076	0.29753161	0.59048994
O	0.41003143	0.07477759	0.57335934
O	0.69688455	0.83167995	0.54457959
O	0.07819024	0.56390627	0.51865683
O	0.55077142	0.32847044	0.48464218
O	0.98437176	0.11390852	0.48060507
O	0.37882346	0.92882344	0.47267699
O	0.74065949	0.71143515	0.45642863
O	0.05018350	0.48384546	0.42621275
O	0.32426284	0.17504907	0.39708975
O	0.73287944	0.97594130	0.39846701
O	0.28227960	0.73178389	0.34599074
O	0.69684912	0.57841570	0.35965241
O	0.99700096	0.33226229	0.33851432
O	0.91130936	0.95480386	0.31980423
Ge	0.73494083	0.97582218	0.82585004
Ge	0.76884277	0.64468452	0.81722938
Ge	0.36477440	0.23632993	0.81283066
Ge	0.06459935	0.63658249	0.72457467
Ge	0.21004267	0.25037952	0.70919503
Ge	0.68673390	0.87092557	0.69429333
Ge	0.38545335	0.26405591	0.60504675
Ge	0.51638401	0.88575938	0.59073316
Ge	0.00734066	0.50737037	0.57638866
Ge	0.70412763	0.90134858	0.48727142
Ge	0.84812599	0.52200203	0.47219638
Ge	0.31642870	0.13563227	0.45691296
Ge	0.01767312	0.53617193	0.36860692
Ge	0.01292377	0.12777886	0.36421472
Ge	0.64831033	0.79664303	0.35557051

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