Persistence and eventual demise of oxygen molecules at terapascal pressures – Supplementary Information

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Supplementary methods

The main searches were performed using the CASTEP plane-wave code [1], ultrasoft pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) [2] Generalized Gradient Approximation (GGA) density functional. For the searches we used a plane wave basis set cutoff of 350 eV and the Brillouin zone integrations were performed with a k-point grid of spacing $2\pi\times0.07$ Å^{-1}. Searches [3] were performed at 0.5, 1, 2, 3, 4, and 5 TPa, with 6, 8, 9, 10, 12 and 16 oxygen atoms per cell (not all combinations of these pressures and numbers of molecules were studied). We relaxed up to 1000 initial structures per system. The final enthalpy-pressure relations were calculated at a higher level of accuracy consisting of harder projector augmented wave (PAW) pseudopotentials with PBE functionals and a basis set cutoff of 900 eV and a k-point grid of spacing $2\pi\times0.030$ Å^{-1} using the VASP code [4]. The phonon and electron-phonon coupling calculations were performed using density functional perturbation theory [5] and the ABINIT code [6]. Troullier-Martins norm-conserving pseudopotentials with a plane-wave cutoff energy of 1633 eV and the PBE-GGA density functional were employed. Large numbers of k-points were sampled to obtain an energy convergence of better than 5×10^{-3} eV. Finally, in order to understand the effects of the exchange-correlation kernel, we have computed the transition pressures between the most favorable phases with several different density functionals.

Supplementary figure

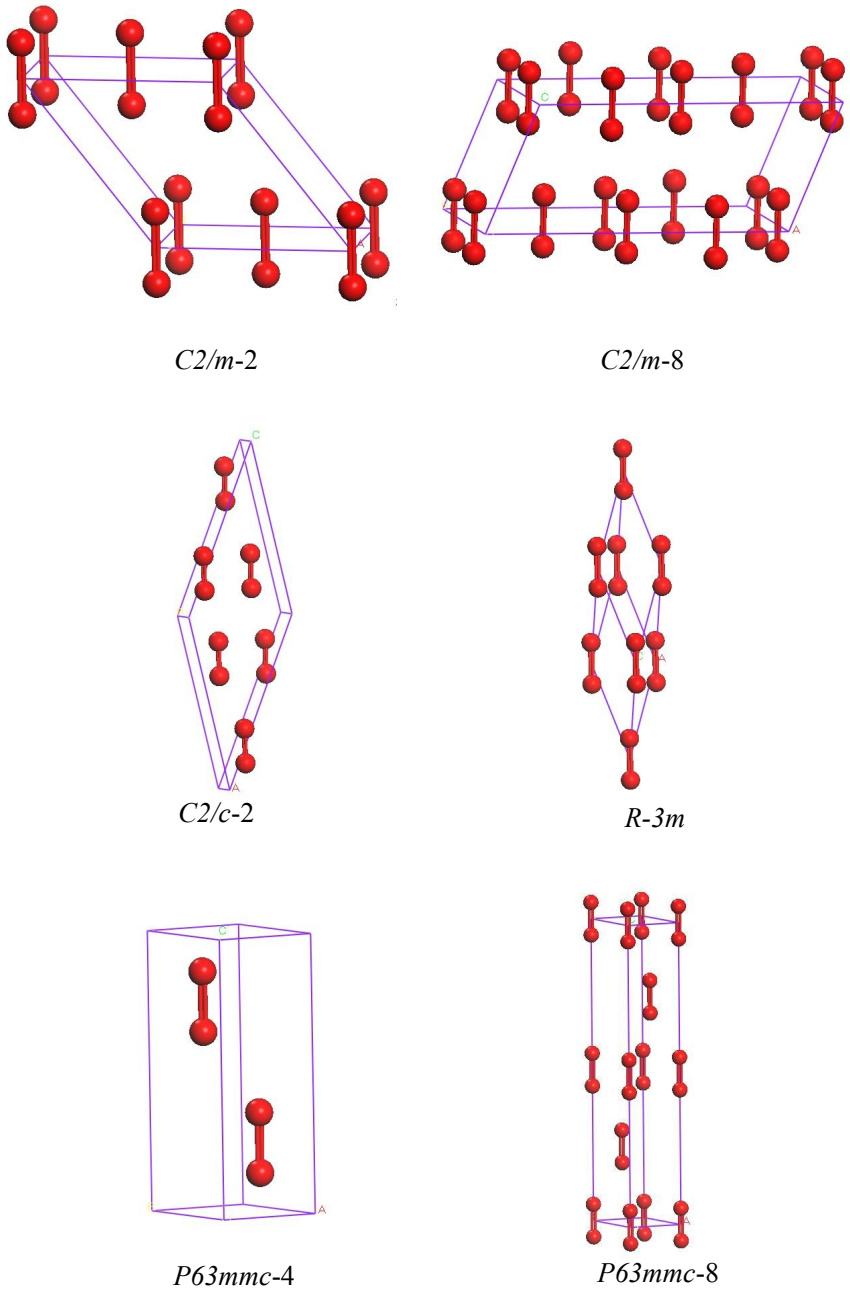
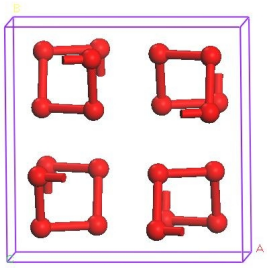
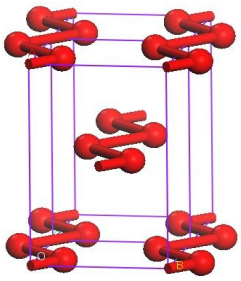


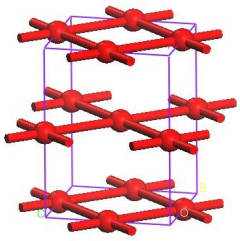
Fig. S1. Crystal structures of the most interesting high-pressure structures of molecular solid oxygen.



I41/acd



Cmcm



Fmmm

Fig. S2. Crystal structures of the most interesting high-pressure structures of polymeric solid oxygen.

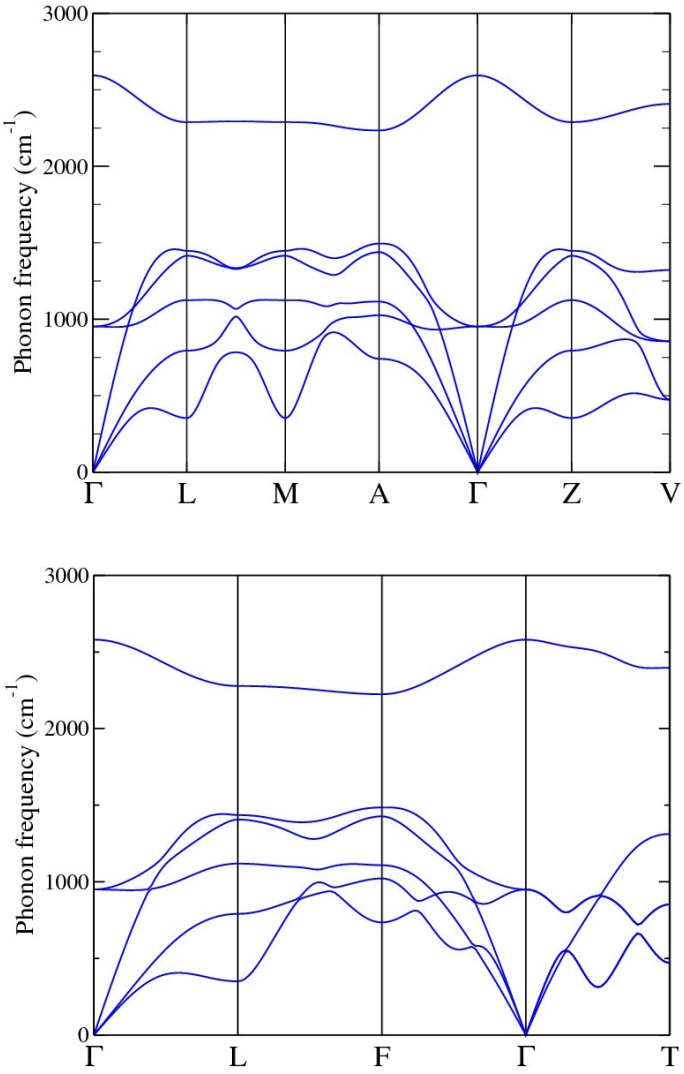


Fig. S3. Phonon dispersion curve of *C2/m* and *R-3m* oxygen at 1.0 TPa with GGA-PBE functional.

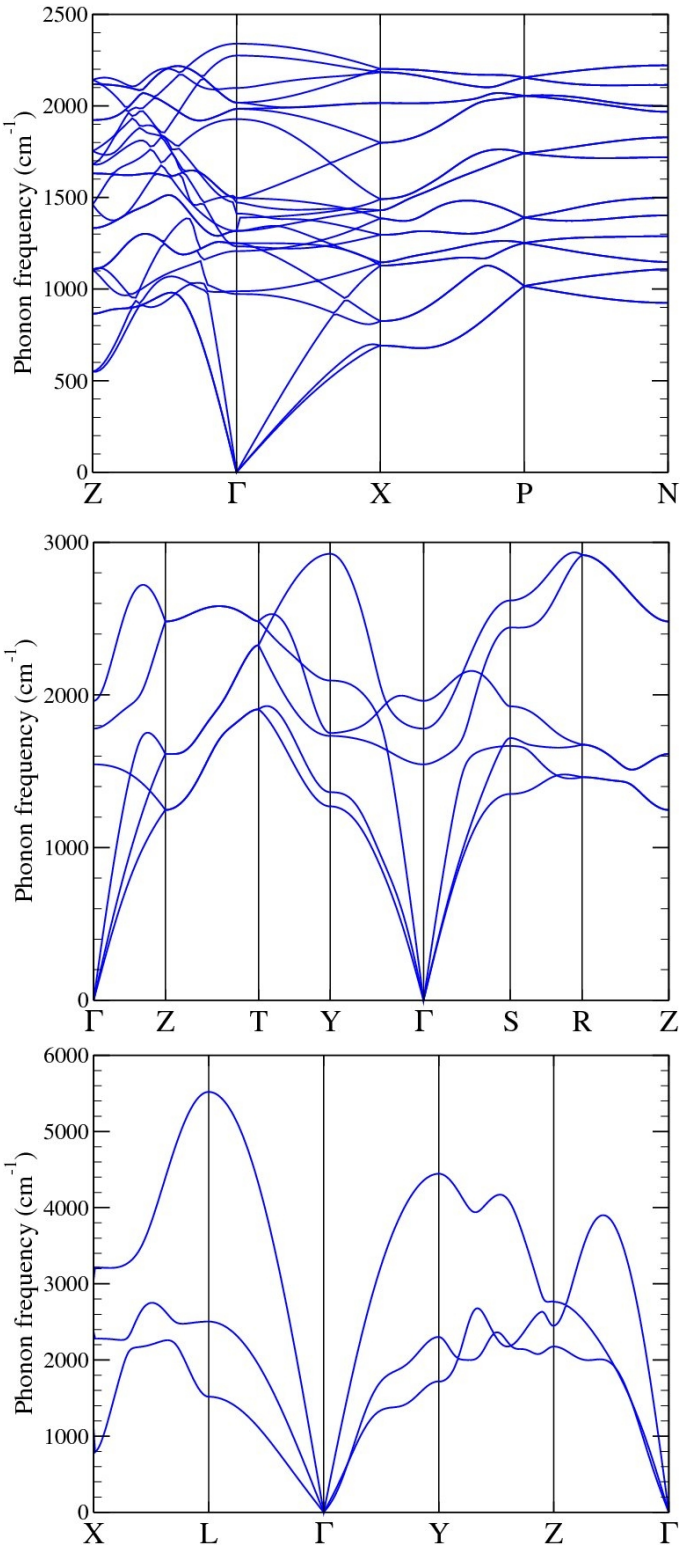


Fig. S4. Phonon dispersion curve of polymeric oxygen with local density approximation (LDA), (a) $I4_1/acd$ at 2 TPa, (b) *Cmcm* at 3.8 TPa, (c) *Fmmm* at 11 TPa.

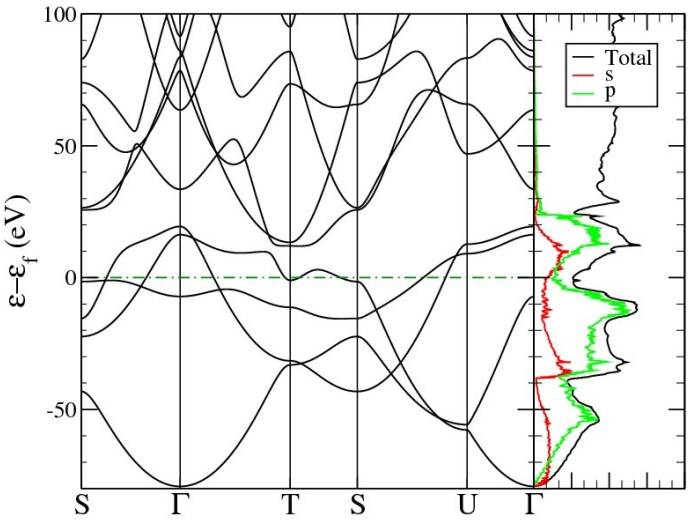


Fig. S5. Electronic band structure and density of states of *Fmmm* at 10 TPa.

Table I. Lattice parameters and atomic positions of the most interesting high-pressure structures of solid oxygen optimized with the PBE functional, the PAW method, and the VASP code [4].

Space group #unit	Pressure (TPa)	Lattice parameters (Å; °)	Atomic coordinates (fractional)
C2/m-2	1.0	2.949 1.702 3.181 α=90.00 β=128.20 γ=90.00	O1 0.1439 0.0000 -0.7843
C2/m-8	0.25	6.807 3.940 3.056 α=90.00 β=68.07 γ=90.00	O1 0.5341 -0.2455 0.7967 O2 0.2114 0.0000 0.2034 O3 0.2796 0.0000 0.7966
C2/c-2	0.25	5.789 1.962 7.298 α=90.00 β=152.68 γ=90.00	O1 -0.3634 -0.0222 -0.2151
R-3m	1.0	2.685 2.685 2.685 α=36.96 β=36.96 γ=36.96	O1 0.9281 0.9281 0.9281
P63mmc-4	1.0	1.702 1.702 5.000 α=90.00 β=90.00 γ=120.0	O1 0.3333 0.6667 0.8579
P63mmc-8	1.0	1.702 1.702 10.000 α=90.00 β=90.00 γ=120.0	O1 0.0000 0.0000 0.0539 O2 0.3333 0.6667 0.3039
$I4_1/acd$	2.0	4.650 4.650 1.802 α=90.00 β=90.00 γ=90.00	O1 -0.1359 -0.1359 -0.2500
Cmcm	3.5	2.675 1.699 1.718 α=90.00 β=90.00 γ=90.00	O1 0.0000 -0.2013 -0.2500
Fmmm	10	2.313 1.412 1.567 α=90.00 β=90.00 γ=90.00	O1 0.5000 0.5000 -0.5000

Table II. Comparison of transition pressures (TPa) with different functionals. US denotes ultrasoft pseudopotentials, PAW denotes the projector augmented wave method, and WC denotes the Wu-Cohen functional [7].

functionals	*R-3m – I41/acd*	*I41/acd - Cmcm*	*Cmcm - Fmmm*
GGA-PBE-PAW (VASP)	1.92	3.00	9.30
GGA-PW91-PAW (VASP)	1.91	2.99	9.66
LDA-PAW (VASP)	1.91	2.71	9.19
GGA-WC-US (CASTEP)	1.83	2.85	8.86

References for Supplementary Information

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