Pressure-induced second-order phase transition in fluorine

Supplementary Material

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This supplementary material contains some auxiliary informations and figures to the main text.

1. Gaussian Basis set - CRYSTAL17

We used the following TZVP basis set in all our calculations [1], here presented in CRYSTAL17 format.

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9 8
0 0 6 2.0 1.0
 35479.100441 0.21545014888E-03
 5318.4728983 0.16700686527E-02
 1210.4810975 0.86733211476E-02
 342.85518140 0.35049933175E-01
 112.01943181 0.11165320133
 40.714740248 0.25988506647
0 0 2 2.0 1.0
 16.043087032 0.39422966880
 6.5321300268 0.24998238551
0 0 1 0.0 1.0
 1.5988881515 1.0000000000
0 0 1 0.0 1.0
 0.69433443154 1.0000000000
0 1 1 0.0 1.0
 0.28000000000 1.0 1.0
0 2 4 5.0 1.0
 89.322913079 0.63685999134E-02
 20.934929831 0.44303143530E-01
 6.5143926757 0.16867248708
 2.3716075957 0.36166346255
0 2 1 0.0 1.0
 0.87224572628 1.0000000000
0 3 1 0.0 1.0
 1.4000000000 1.0000000000
99 0
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2. Convergence tests - CRYSTAL17

Convergence tests were performed to evaluate the effect of the main CRYSTAL settings for structure optimization on the α-F_2 $C2/c$ crystal structure, namely TOLDEG, TOLDEX, and MAXTRADIUS. TOLDEG defines the tolerance for the root-mean-square of the energy gradient in each self-consistent field cycle. The potential energy surface (PES) of molecular crystals often exhibits a flat landscape, so very tight tolerances on the gradient must be used. Otherwise, the algorithm may converge prematurely. The tolerance on the maximum gradient component is 1.5 times the value of TOLDEG. TOLDEX defines the root-mean-square threshold for atomic displacements for the optimization cycles. Just as with TOLDEG, the maximum tolerance for an atomic displacement is 1.5 times the value of TOLDEX. Lastly, the MAXTRADIUS keyword defines the maximum trust radius allowed in search of the minimum in the potential energy surface. This parameter, whose default value is 4.0 in CRYSTAL17, is essential for optimizing the structure of molecular crystals having a flat energy hypersurface. The trust region is the region of the objective function (the potential energy, in our case) that will be approximated by a simpler (usually quadratic) model. The step size of the optimization algorithm (changes in lattice parameters and atomic positions in our case) varies inversely proportional to the curvature (the Hessian, in higher dimensions) at the current position on the energy hypersurface. In flat regions with small curvature, the step size tends to be large, and the algorithm may miss a minimum due to an oversized step. MAXTRADIUS limits the size of the step in the minimization algorithm. However, reducing MAXTRADIUS comes with the risk of a slower convergence of the optimization algorithm. We tested the convergence of the energy and the structural parameters after optimization by varying TOLDEG (3×10^{-5}, 10^{-5}, and 5×10^{-6}),

TOLDEX (1.2×10^{-3}, 5×10^{-5}, and 10^{-5}), and MAXTRADIUS (0.25, 0.1, and 0.05). Notice that even the least strict conditions tested are already much more stringent than the default values (3×10^{-4}, 1.2×10^{-3}, and 4.0 for TOLDEG, TOLDEX, and MAXTRADIUS, respectively). In fact, we chose to be rigorous in this aspect precisely because we are dealing with a molecular crystal with a possibly flat energy hypersurface around the global minimum. The optimization convergence tests were performed using the experimentally determined structure for α-F_2 relaxed using the default CRYSTAL17 optimization parameters as the starting point, which is the same $C2/c$ fluorine crystal structure of minimum energy found by USPEX at P=0.

3. Static stability - CRYSTAL17

We chose very strict convergence criteria for crystal structure optimization of fluorine $C2/c$ and $Cmce$ phases, namely TOLDEG 0.00001, TOLDEX 0.0001, TOLDEE 11, and MAXTRADIUS 0.01. For the calculation of the static energies of the optimized structures, the chosen conditions were XXLGRID, TOLDEE 12, TOLINTEG 10 10 10 20 40, and SHRINK 11 11 5. These conditions were chosen to ensure an energy convergence within $1.5\,\mu E_\mathrm{h}$/atom, which is actually smaller than the expected accuracy of DFT calculations (see below). Furthermore, these same conditions were also employed in obtaining the parameters of the Vinet equation of state for the $C2/c$ fluorine crystal structure.

4. Lattice parameters and atomic positions
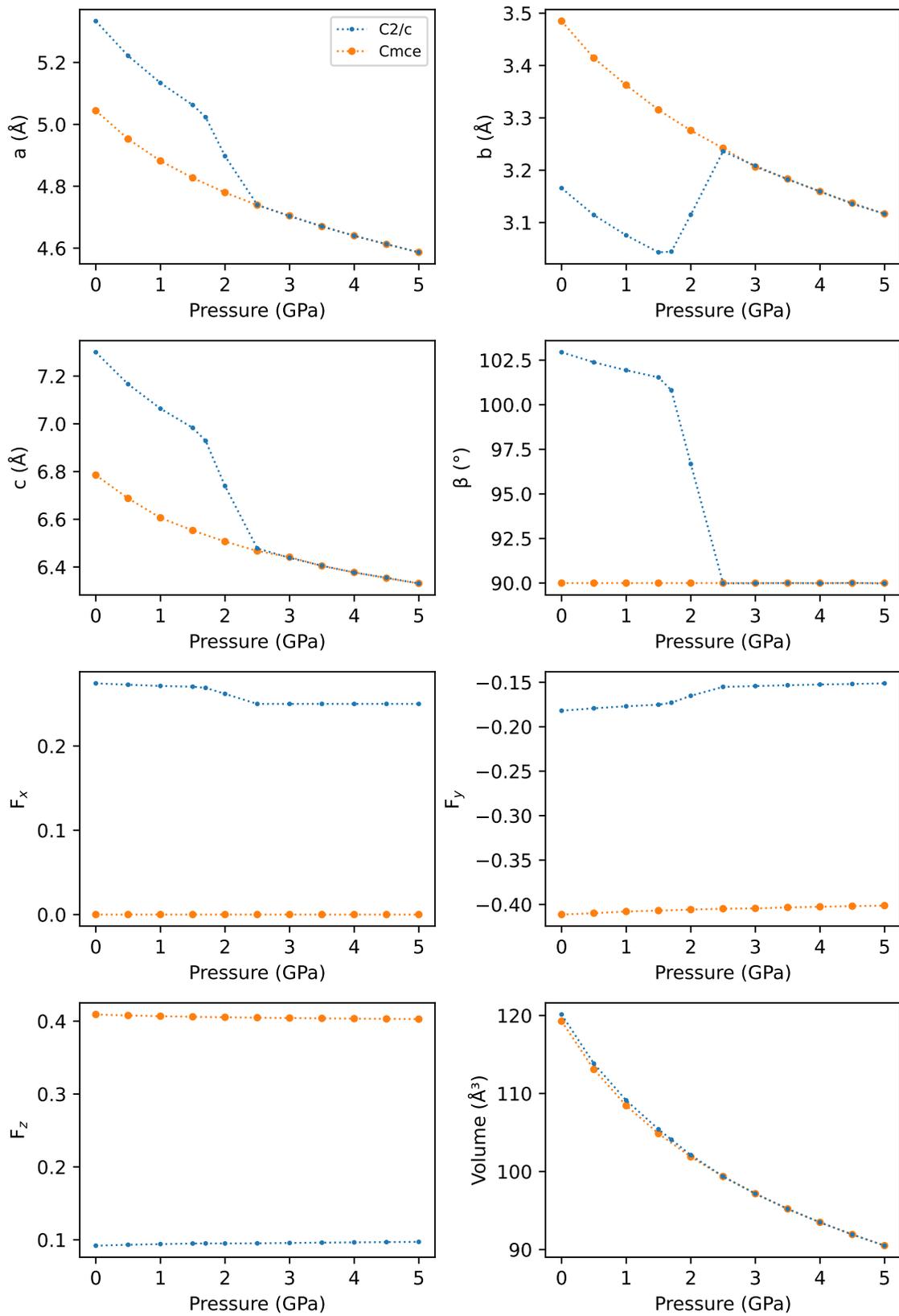
Figure S1: Lattice parameters and atomic positions of the fluorine structures as a function of the pressure imposed in the optimization. The constant pressure optimization minimizes the static enthalpy (no zero-point energy)

5. Contributions to Total Energy
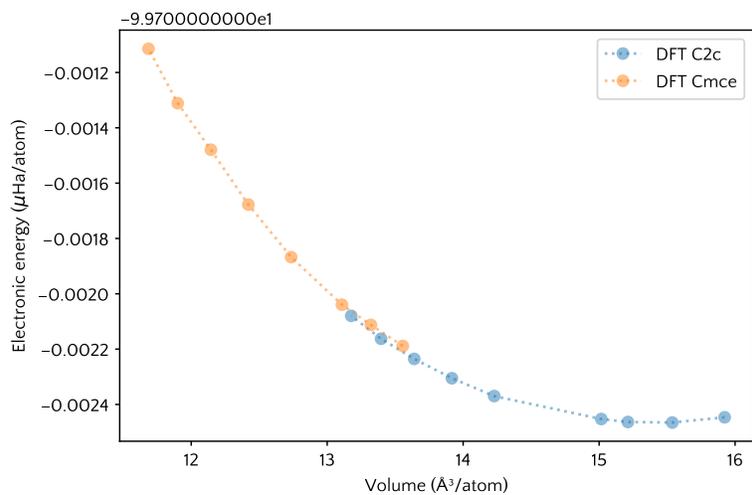
(a) Electronic (potential) energy.
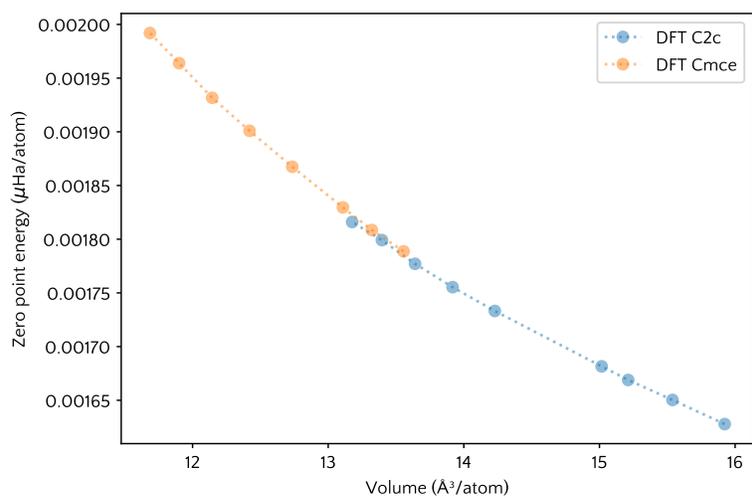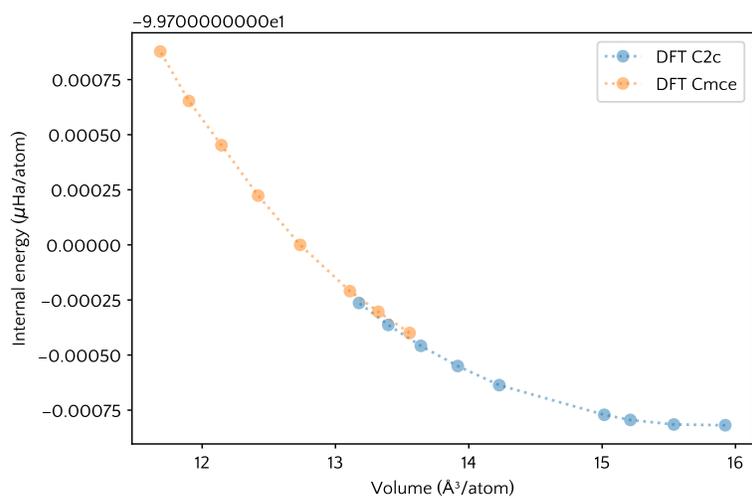
(b) Zero point energy.

(c) Internal energy.

Figure S2: Contribution to total energy as a function of volume. Circles are the DFT data calculated at the PBE0+D3(ABC)/TZVP level of theory. Dotted lines are a guide to the eyes.
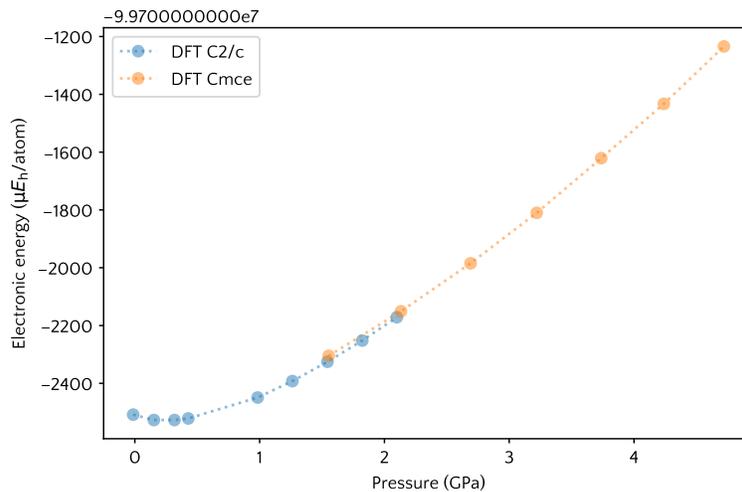
(a) Electronic (potential) energy.
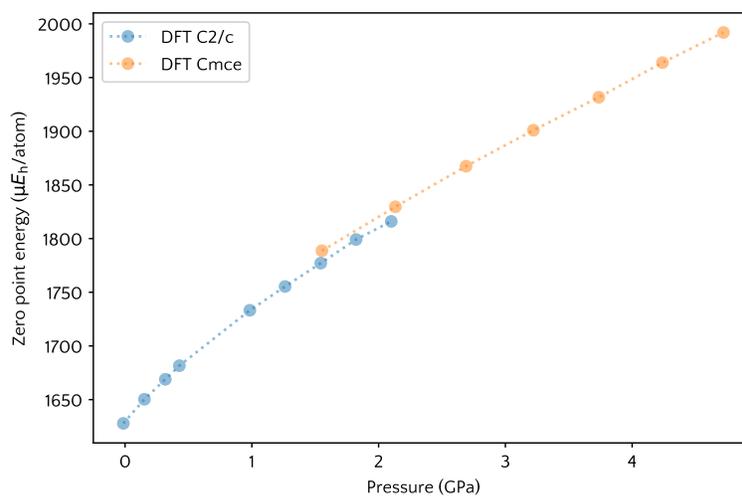
(b) Zero point energy.
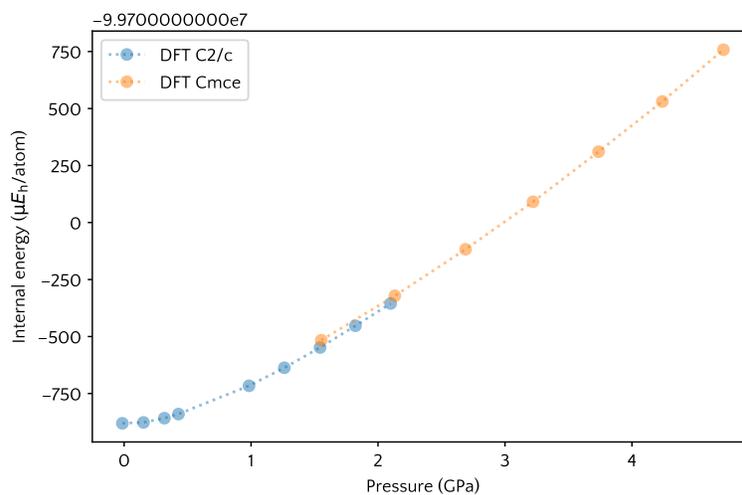
(c) Internal energy.

Figure S3: Contributions to total energy as a function of pressure. Circles are the DFT data calculated at the PBE0+D3(ABC)/TZVP level of theory. Volume was converted to pressure for each phase using their respective fitted Birch-Murnahan equation of state. Dotted lines are a guide to the eyes.

6. Dynamical stability - Unstable modes
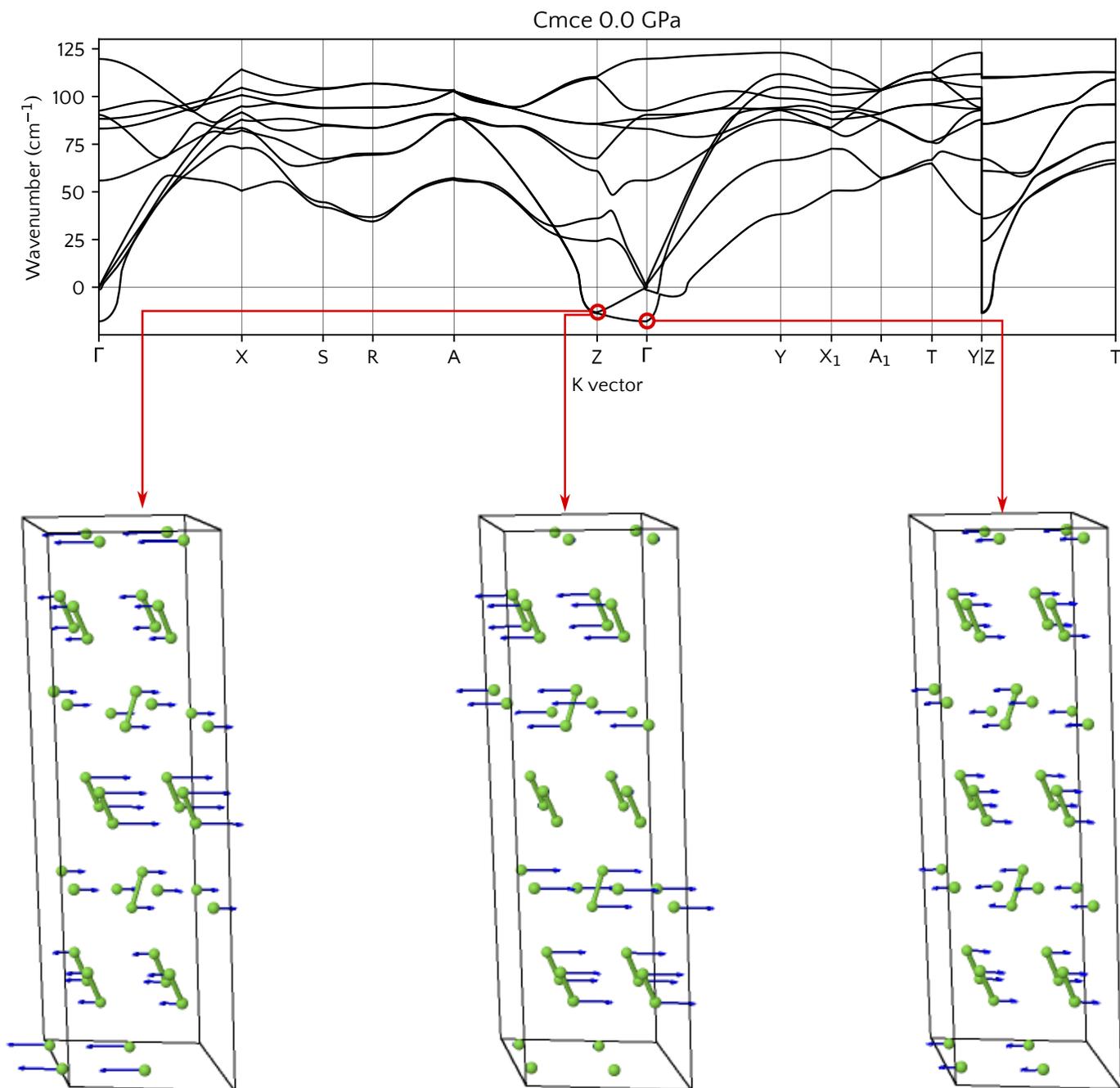
Figure S4: Phonon dispersion spectra for the fluorine Cmce structure at 0 GPa with representations of their eigenvectors on an expanded $1 \times 1 \times 2$ primitive cell. All eigenvectors have null c (z) components, meaning that they represent oscilations of pure shear deformation between the layers of molecules. It should also be noted that the fluorine atoms in their respective molecule move as a single entity.

7. Dynamical stability - Potential of unstable mode at Γ
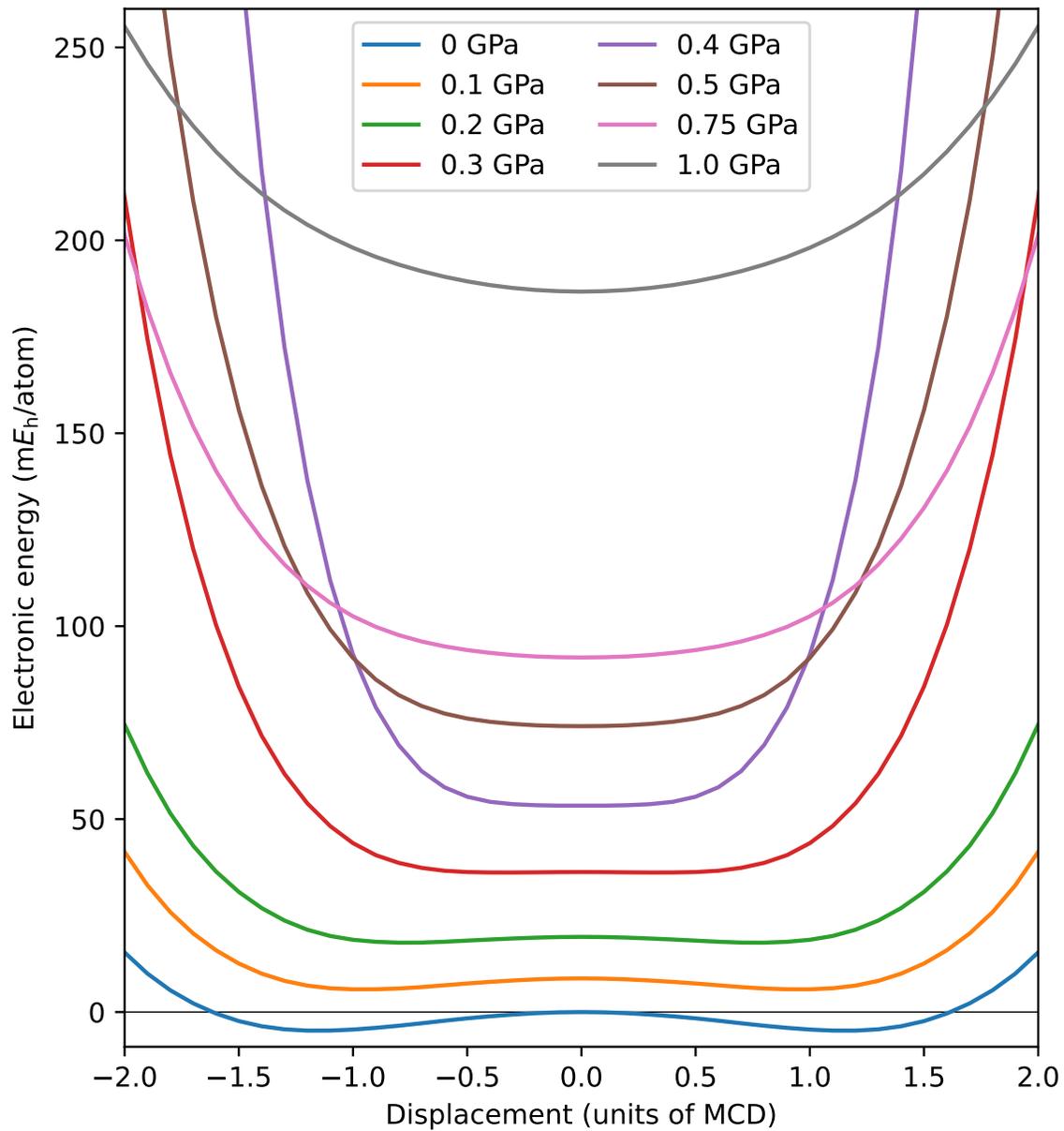
Figure S5: Potential energy *versus* displacement along the eigenvector of the Γ-point mode of imaginary frequency for the orthorhombic *Cmce* fluorine structure at different pressures. MCD stands for Maximum Classical Displacement [2].
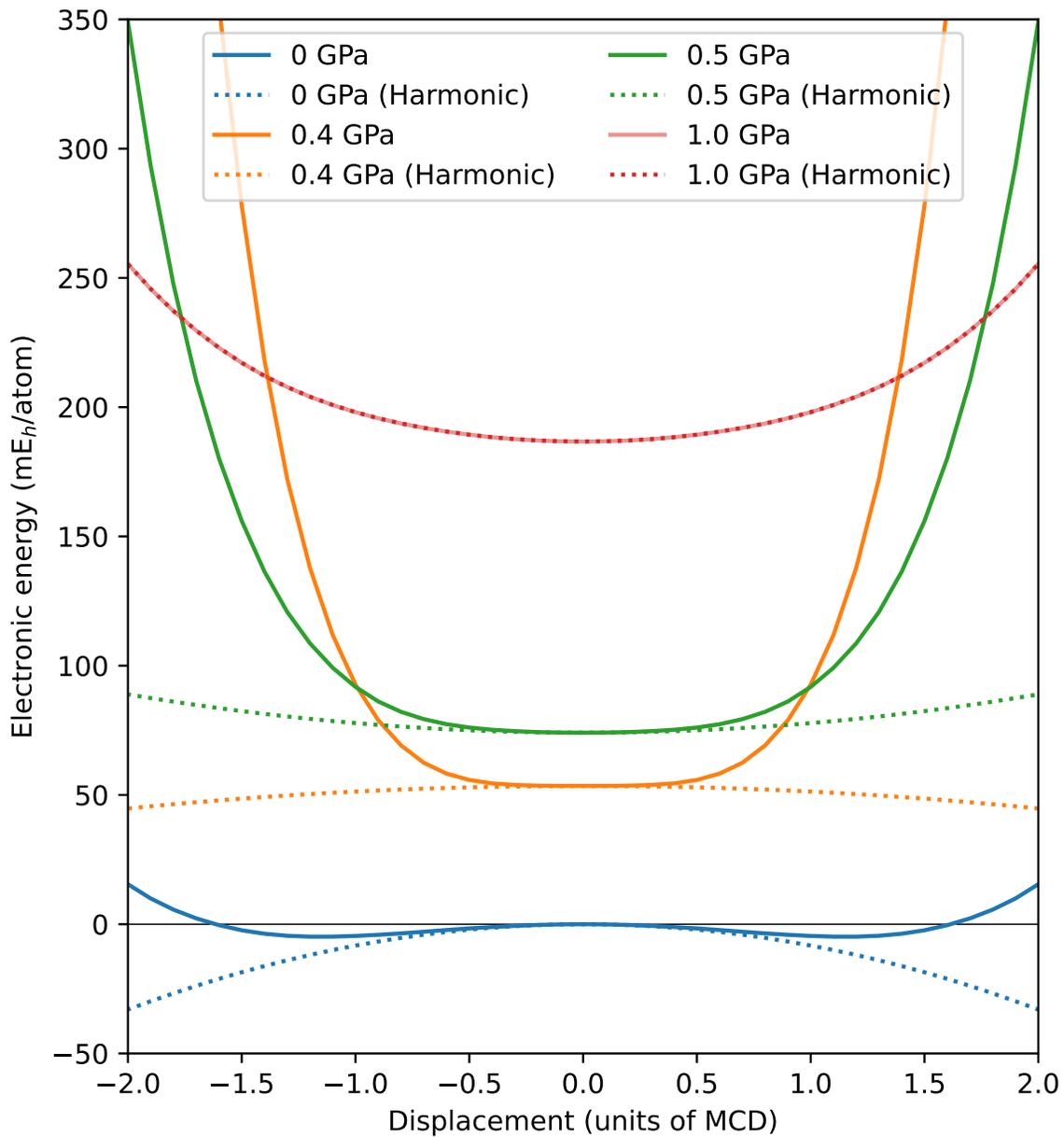
Figure S6: Potential energy *versus* displacement along the eigenvector of the Γ-point mode of imaginary frequency for the orthorhombic *Cmce* fluorine structure at different pressures compared to the respective harmonic potential. Notice that a proper description of this mode in the *quasi*-harmonic approximation is only possible above 1.0 GPa. MCD stands for Maximum Classical Displacement [2].

References

[1] S. Mattsson, B. Paulus, F. A. Redeker, H. Beckers, S. Riedel, C. Müller, The Crystal Structure of α-F$_2$: Solving a 50 Year Old Puzzle Computationally, Chem. Eur. J. 25 (13) (2019) 3318–3324.

[2] R. Dovesi, V. Saunders, C. Roetti, R. Orlando, C. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. Harrison, I. Bush, et al., CRYSTAL17 User's Manual .