

**Supporting Information for “Thermodynamics of the Flexible
Metal-Organic Framework Material MIL-53(Cr) From First
Principles”**

Eric Cockayne

*Materials Measurement Science Division, Material Measurement Laboratory,
National Institute of Standards and Technology,
Gaithersburg, Maryland 20899 USA*

The DFT calculations were performed using the codes VASP 5.3.3 and VASP 5.4.1. VASP 5.2 PAW-PBE pseudopotentials were used for the ions, with 12, 6, 4, and 1 valence electrons for Cr, O, C, and H, respectively. A plane wave cutoff of 500 eV was used. The same 2x2x2 Monkhorst-Pack grid of k-points was used for all unit cells. It was verified that energies were converged with respect to the k-point sampling to better than 0.01 kJ mol⁻¹, even for the smallest unit cell considered. The lowest-energy magnetic states had alternating spins for Cr along the same Cr-OH-Cr chain. Generally, alternating Cr-OH-Cr chains linked by bdc linkers preferred an antiferromagnetic ordering of spins at the same crystallographic *c* value. Some large-unit-cell structures were very slightly lower in energy with a ferromagnetic ordering of these spins, but this spin arrangement led to poor convergence at low volumes, so the same “AFM” spin arrangement was used for all calculations.

The choice of Hubbard *U* and *J* parameters was determined by matching the experimental bandgap and minimizing the residual forces on the experimental crystal structure of corundum Cr₂O₃. For the GGA calculations, the use of a *U* value for O led to little improvement. For the metaGGA calculations, *U* for O was set to 7.05 eV, and the Cr *U* reoptimized to again fit the bandgap. The large oxygen *U* value was set in anticipation of further computational studies of the interaction of water with MIL-53 (Cr). It had previously been found that excellent results for small water clusters were obtained using metaGGA calculations with this value of *U*.

Phonon *anharmonicity* can influence the phonon entropy. It is difficult to quantitatively calculate the entropy of a single anharmonic oscillator, let alone anharmonic coupling between modes. In this work, we use the effective entropy of anharmonic modes in the following semiquantitative way. First, we neglect coupling, and only consider intramode anharmonicity. Phonon anharmonicity was found to be insignificant for all modes with frequencies above 75 cm⁻¹. For modes with $\nu_\mu < 75$ cm⁻¹, the potential energy versus amplitude $\Delta U_\mu(x_\mu)$ was calculated for eleven different amplitudes via DFT and fit to an eighth-order polynomial. For a purely harmonic mode,

$$\Delta U_\mu = 2\pi^2(m_{\text{eff}})_\mu(V)\nu_\mu^2(V)x_\mu^2, \tag{1}$$

where $(m_{\text{eff}})_\mu(V)$ is the effective mass. For an anharmonic mode,

$$\Delta U_\mu = 2\pi^2(m_{\text{eff}})_\mu(V)\nu_\mu^2(V)x_\mu^2 + \dots \tag{2}$$

We use the partition theory to estimate the representative fluctuation of a phonon mode at temperature T , $\Delta U_\mu = k_B T/2$, and from the polynomial fit, the representative amplitude x_μ . We then evaluate

$$k_B T/2 = 2\pi^2(m_{\text{eff}})_\mu(V)\nu_\mu^2(V)x_\mu^2 + \dots = 2\pi^2(m_{\text{eff}})_\mu(V)\nu'_\mu{}^2(V,T)x_\mu^2 \quad (3)$$

to find the effective frequency of the anharmonic mode $\nu'_\mu(V,T)$. Finally, the contribution of this anharmonic mode to the thermodynamic functions was estimated by using $\nu'_\mu(V,T)$ instead of $\nu_\mu(V)$ in Eq. (1)-(3) of the main text.

The rank-ordering of the phonon frequencies was always done for the $\nu'_\mu(V,T)$. Unexpectedly, the phonon calculations for $V = 1506 \text{ \AA}^3$ yielded a shallow 25 i cm^{-1} instability. The displacement pattern of this instability is the same bdc rotational type that occurs between the lp and the np structures, but, at fixed volume, the relaxation to one of the double well bottoms only lowers the total energy about 0.1 kJ mol^{-1} with respect to the reference structure. In practice, the anharmonicity of this unstable mode was treated in the same way as for the other low-frequency modes, and renormalization led to a positive frequency. The relaxation of this mode explains the slight deviation of β from 90° within the orthorhombic phase seen in main text Fig. 6. In actuality, thermal fluctuations should lead to an average structure with $\beta = 90^\circ$

Because of the weak divergence in Eq. (1-2) of the main text as $\nu \rightarrow 0$, it may be possible that differences in the acoustic phonon branches near the origin that are necessarily neglected in a supercell calculation could have a large effect on the results. Not knowing a priori the magnitude of this effect, we estimated and included the contribution of acoustic phonons to the thermodynamics as follows. The lowest frequency optical modes were treated as if they belonged to the unfolded acoustic branches of the most primitive cell. (Phonon eigenvectors were not checked to verify if they were actually “acoustic-like”.) Eigenmodes 4, 5, and 6 were used to estimate the lowest-frequency acoustic branch. It was assumed that the acoustic branches connected the Brillouin zone origin with modes 4, 5, and 6 in the unfolded scheme along directions \mathbf{b}_1 , \mathbf{b}_2 and \mathbf{b}_3 respectively, where \mathbf{b} are the supercell reciprocal lattice vectors. The acoustic mode frequency within the first Brillouin zone at $\mathbf{q} = q_1\mathbf{b}_1 + q_2\mathbf{b}_2 + q_3\mathbf{b}_3$ was estimated via linear interpolation as $\nu(\mathbf{q}) = q_1\nu_4 + q_2\nu_5 + q_3\nu_6$. In the first Brillouin zone, q_1 , q_2 and q_3 range from $-1/2$ to $1/2$. Eq.(2) of the main text was numerically integrated throughout the Brillouin zone using $\nu(\mathbf{q})$ as the frequency. The

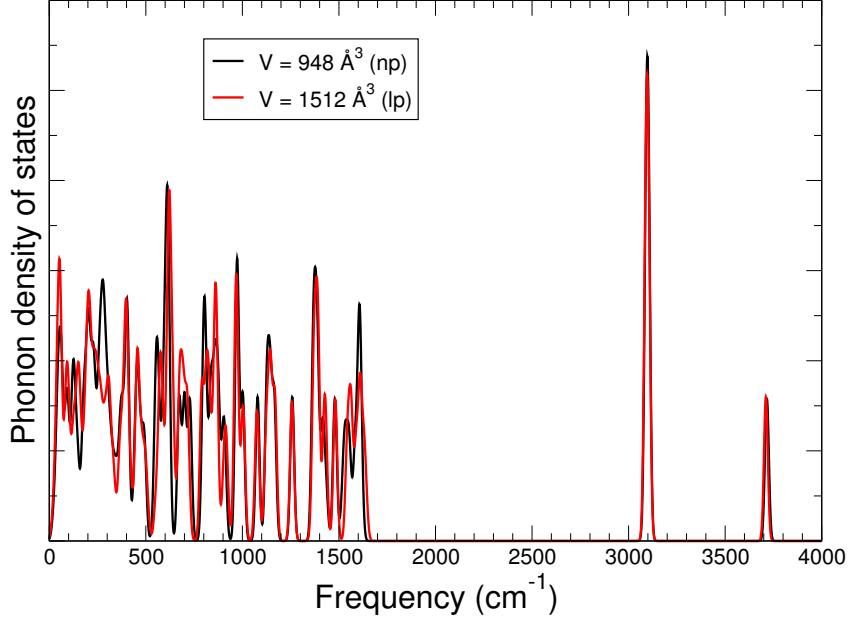


FIG. S1. Calculated phonon density of states of MIL-53(Cr) for the *np* and *lp* phases.

other two acoustic branches were treated similarly, interpolating from modes 7, 8, 9 and 10, 11, 12, respectively. In the end, the contribution of the acoustic branches near the origin was estimated to enhance the free energy of the *lp* phase about 1.5 kJ mol^{-1} with respect to the *np* phase at room temperature, about 15 % of the total.

The first physical motivation for the phonon interpolation formula Eq. (3) in the main text is that force constants, proportional to phonon frequencies squared, are a more fundamental quantity to interpolate than the frequencies themselves. The second physical motivation is consideration of the large and small volume limits. As V goes to zero, all phonon frequencies should diverge. As V goes to infinity, under periodic boundary conditions, the structure should break up in non-interacting molecules and the intramolecular frequencies should become constant and the other frequencies zero. Therefore, we choose a form for ν^2 that in terms of a constant and positive powers of $(1/V)$. In interpolating the $V = 1200 \text{ \AA}^3$ phonon results from the $V = 710 \text{ \AA}^3$ and $V = 1506 \text{ \AA}^3$ results using fits terms of the form $C + (1/V^p)$, the best fit was for p near the integer 2. It was natural to add a term of the form $(1/V)$ for the three-parameter fits.

The calculated phonon density of states (DOS) for MIL-53(Cr) at room temperature in the *np* and *lp* phases are shown in Fig. S1 and Fig. S2. The phonon fingerprints are largely similar, except for slight frequency shifts and for changes due to the hydrogen “flopping”

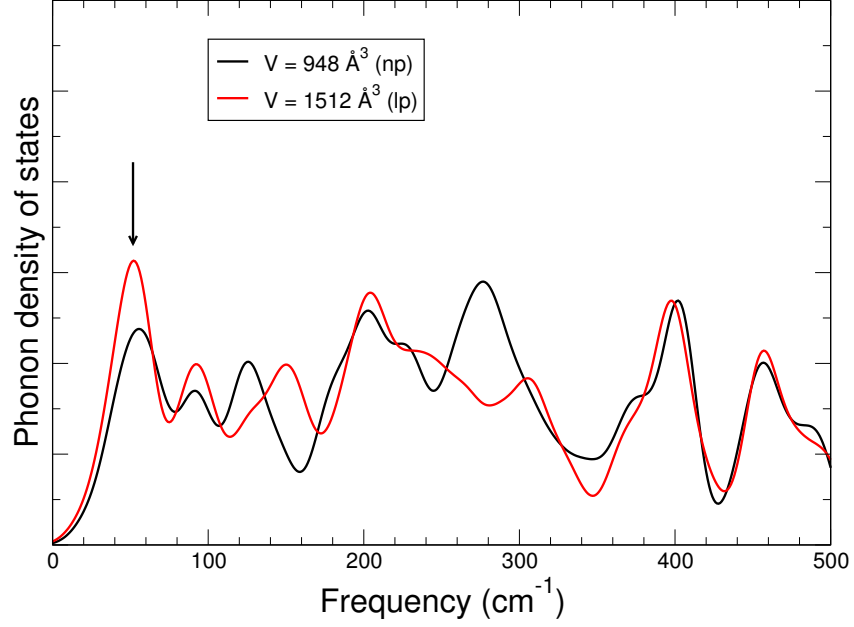


FIG. S2. Same as Fig. S1, for phonons with frequencies below 500 cm^{-1} . The arrow indicates the enhancement of the low-frequency DOS for the *lp* phase relative to the *np* phase.

mode discussed in the main text. The DOS at low frequency modes show a stronger peak around 52 cm^{-1} for the *lp* phase than for the *np* phase (indicated by the arrow in Fig. S2). This change in the DOS at low frequencies is the strongest contributor to reducing the free energy of the *lp* phase relative to the *np* phase.