# Isomorphism between ice and silica: Supplementary Information

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February 12, 2010

# 1 A comparison between TIP4P energetics with DFT

Although the TIP4P/2005 is explicitly fitted to reproduce the phase diagram and is thus undoubtedly a very sensible way to model the dense ice phases it is questionable whether this rather simplistic potential will be able to capture the more subtle energetics of more exotic empty, hypothetical clathrate hydrates. Work already has already been carried out on modeling methane hydrate and other empty clathrate structures [1, 2] with this potential and it has been shown to perform well in these situations. Nonetheless, to assure ourselves of the verity of this approach the total energy gamma point optimizations of some of the ice structures with smaller unit cells that were examined in this work have been carried out using the PW91 functional, implemented in CASTEP [3] with a plane wave cutoff of 500 eV. The correlation between the energetics obtained from DFT and from the potential is shown in figure 1

As discussed in a recent paper by Conde *et. al* [4] figure 1 shows that DFT overestimates the energies of all the investigated phases. What is more the potential is known to accurately reproduce the experimental phase diagram for these phases, which indicates that the potential provides a better description of the chemistry than DFT. It would seem then that hard constraining the HOH angle (which the rigid body TIP4P model does) is a reasonable approximation. It should be pointed out however that DFT and the potential produce the same
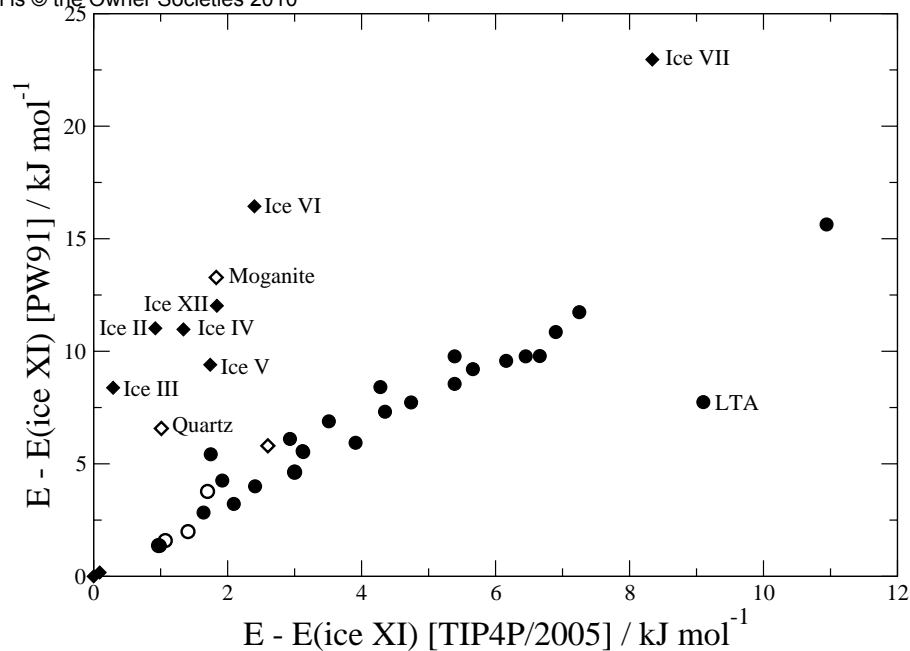
Figure 1: Comparison of the energetics of the ice phases calculated using TIP4P/2005 and the PW91 functional. Filled circles are hypothetical (for ice) topologies based on zeotypes from the atlas of framework zeolite types, empty circles are the currently known clathrates, empty squares are the dense ice phases and filled squares the dense silicates.

energetic ordering for the dense phases.

For the hypothetical phases there is a strong correlation between the energies calculated using the potential and those calculated using DFT (although DFT again overestimates energy differences with respect to the potential). This suggests that the results of this paper would not be greatly changed if the calculations were done at the "higher level of theory".

# 2 A comparison of the FFSiOH energetics with known silica thermochemistry

High-temperature lead borate solution calorimetry was performed by Navrotsky and co-workers on 13 all-silica zeolites and three dense silica polymorphs to obtain enthalpies of transition at 298 K [5]. This quantity is indicative of a materials stability at room temperature as entropic differences between siliceous materials are known to be small. Reproducing these energetics is a more stringent test on a potential or DFT than reproducing the phase diagram as information is included on phases that are metastable and hence do not appear on the phase diagram.

The calculation that would most closely mirror the experiment would be a minimization of the Gibbs free energy of a siliceous material to obtain the equilibrium structure at 298 K followed by a single point enthalpy calculation including the vibrational contribution to the internal energy. However, it is unclear how one would best minimize the Gibbs free energy at 298 K as probably this is outside the relatively small range of temperatures at which the harmonic approximation is applicable. In addition potentials are commonly fitted so as to reproduce the high temperature observables at 0 K.
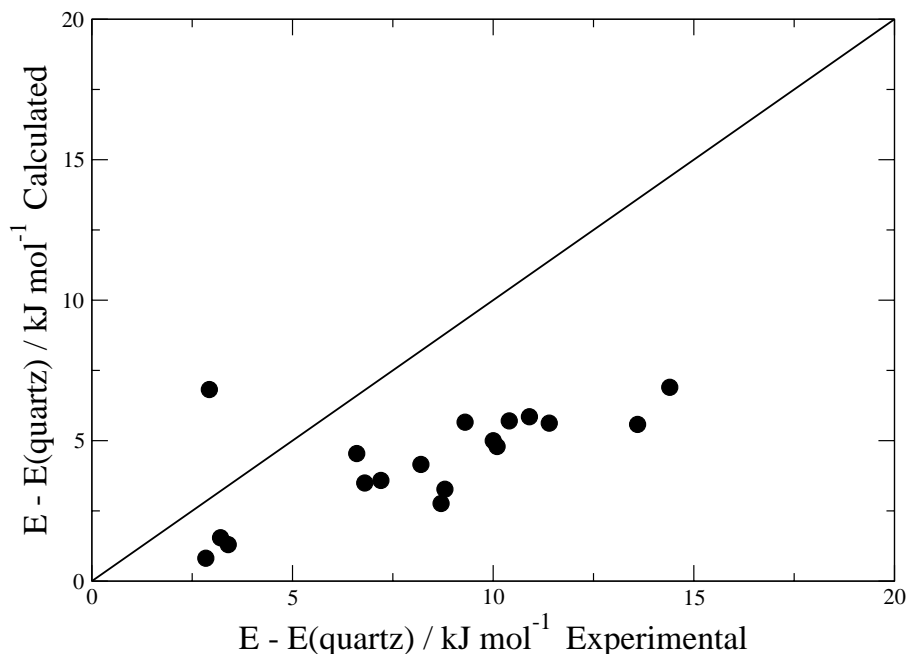


Figure 2: Comparison of the energies of various ice phases relative to quartz obtained from thermochemical analysis with the models used to describe silica in our paper.

In figure 2 we compare the experimental enthalpies relative to quartz with those obtained from the FFSiOH potential. Much like what was was found for the Gale-Sastre and Sanders-Leslie-Catlow potentials [6] the FFSiOH potential reproduces the energetic ordering found from in the thermochemical data. However, the potential consistently underestimates the energy differences but this will not affect the results of the paper. It is interesting to compare this analysis with the B3LYP calculations on these phases in reference [6] as this functional is seen to overestimate the differences in energies between phases.

The only structure whose energy is not well described by the potential is coesite. This would explain why the transition pressure from quartz to coesite is overestimated in the calculations.

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# 3   Equilibrium pressures calculated using the 0 order approximation

The pressures at which the phases that appear on the phase diagram for ice and silica with the other phases examined in this work would be at equilibrium has been calculated using the zero order approximation described in the text. None of the hypothetical phases (except the silica analogue of ice VI) have a transition pressure to one of the known phases in the stability range of that phase. Hence, all these structures would, if formed, be metastable.

|          | Tridymite | Cristobalite | Quartz  | Coesite | Stishovite |
|----------|-----------|--------------|---------|---------|------------|
| Ice II   | 1.787     | 2.334        | 10.501  | -10.305 | 7.443      |
| Keatite  | 1.463     | 4.411        | -1.475  | 0.604   | 5.450      |
| Ice IV   | 3.591     | 4.219        | 8.789   | 12.655  | 7.170      |
| Ice V    | 1.415     | 1.827        | 6.077   | 29.223  | 8.357      |
| Ice VI   | 2.987     | 3.492        | 6.855   | 8.624   | 8.842      |
| Ice VII  | 8.988     | 10.030       | 16.125  | 20.431  | -16.360    |
| Ice XII  | 3.946     | 4.810        | 13.913  | 55.046  | 5.904      |

Table 1: Equilibrium pressures (at 0 K) for the silica phases. The horizontal axis of this table contains the phases that appear on the phase diagram while the vertical has on the hypothetical and metastable phases.

|          | Ice Ih | Ice II | Ice VI | Ice VII |
|----------|--------|--------|--------|---------|
| Ice III  | 0.140  | 1.566  | 1.012  | 14.544  |
| Ice IV   | 0.346  | 0.376  | 2.182  | 27.823  |
| Ice V    | 0.388  | 0.675  | 0.947  | 21.659  |
| Ice XII  | 0.293  | 0.169  | 4.542  | 30.396  |

Table 2: Equilibrium pressures (at 0 K) for the known the ice phases. The horizontal axis has on those phases that are stable at 0 K. The vertical has the metastable phases and those phases that only appear at higher temperatures.

|          | Ice Ih | Ice II | Ice VI | Ice VII |
|----------|--------|--------|--------|---------|
| Quartz   | 0.350  | 0.316  | 0.630  | 12.811  |
| Moganite | 1.045  | -0.826 | 0.043  | 11.070  |
| Coesite  | 0.504  | 2.954  | 0.414  | 18.162  |

Table 3: Equilibrium pressures (at 0 K) for the hypothetical ice phases. The horizontal axis has on those phases that are stable at 0 K. The vertical has the hypothetical phases that are analogues to known silicates.

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