Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Anomalous nuclear quantum effects in ice[1] BETÜL PAMUK, Stony Brook University, JOSE M. SOLER, Universidad Autonoma de Madrid, PHILIP B. ALLEN, MARIVI FERNÁNDEZ-SERRA, Stony Brook University — The lattice parameters of light (H_2O) and heavy (D_2O) Ih ice at 10 K differ by 0.09%.[1] The larger lattice constant is that of the heavier isotope. This isotope shift with anomalous sign is linked to the zero point point energy of phonons in ice. To determine the origin of this anomaly, we use *ab initio* density functional theory to compute the free energy of ice within the quasiharmonic approximation. As expected, the frozen lattice constant at T = 0 K is smaller than the quantum lattice constant, independent of the isotopic substitution. We find that, the heavy isotope D gives more zero point expansion than H, whereas the heavy isotope ^{18}O gives normal zero point expansion, i.e smaller than ^{16}O. Relative to the the classical result, the net effect of quantum nuclei (H and O) on volume has the conventional (positive) sign at T = 0 but it becomes negative above 70 K, indicating that it may be also relevant for liquid water. These results are not reproduced by state of art polarizable empirical potentials.[2] [1] B. K. Röttger *et. al.*, Acta Cryst. B **50**, 644-648 (1994). [2] C. P. Herrero and R. Ramírez, J. Chem. Phys. **134**, 094510 (2011).

[1]This work is supported by DOE award numbers DE-FG02-08ER46550, DE-SC0003871.

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Date submitted: 10 Nov 2011 Electronic form version 1.4