Fictitious Allotropes of Crystalline Bromine and Iodine in DFT

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Common density functional theory methods end up at an erroneous ground state for the solid-state structures of the elements bromine and iodine [1]. Phonon calculations at the GGA level of theory for both experimental crystal structures show imaginary modes (see Figure 1).

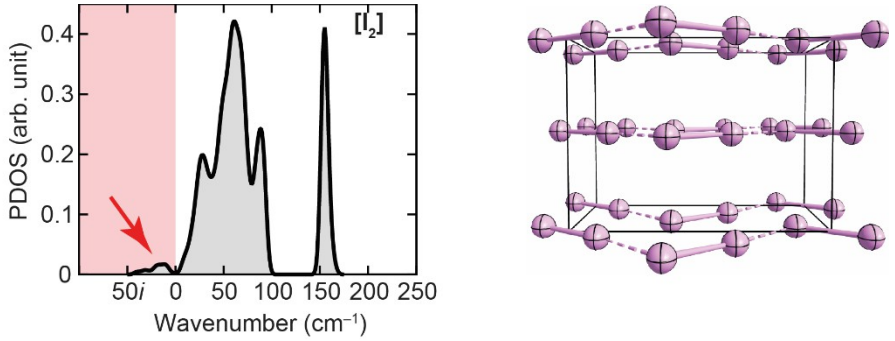

Figure 1. Phonon density of states and structure of solid iodine.

These imaginary modes lead to energetically more favorable and dynamically stable structures, built up from monoatomic chains. Going up the Jacobs ladder of functionals can only partly solve the problem. Some meta GGAs and hybrid functionals yield the correct energetic order for bromine, but not for iodine. Both periodic Hartree-Fock and MP2 arrive at the qualitatively correct result. Efficient DFT functionals perform poorly in these cases. This should be kept in mind when doing global structure prediction with systems significantly stabilized by halogen bonds.

References:

[1] J. George et al., *ChemPhysChem* **16**, *728-732* (2015).