Allotropic halogens.

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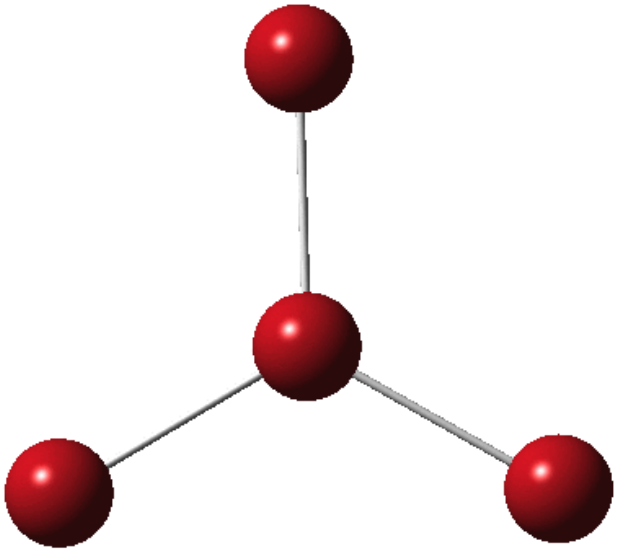
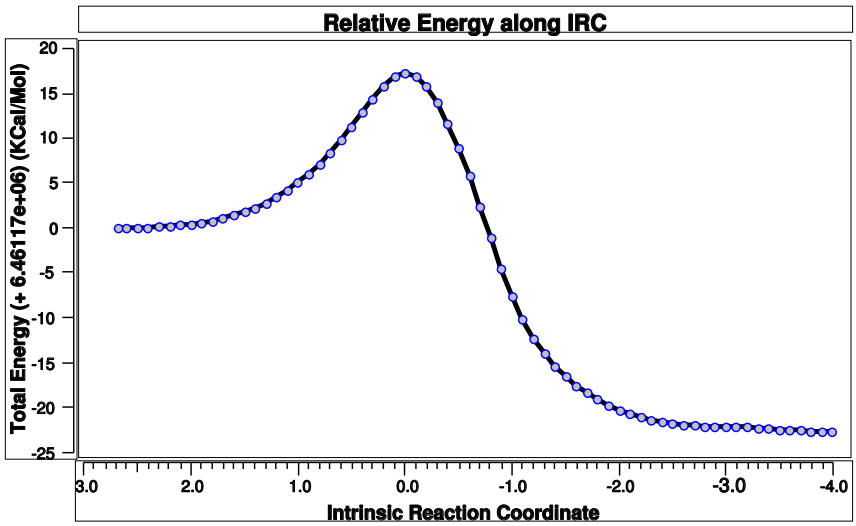
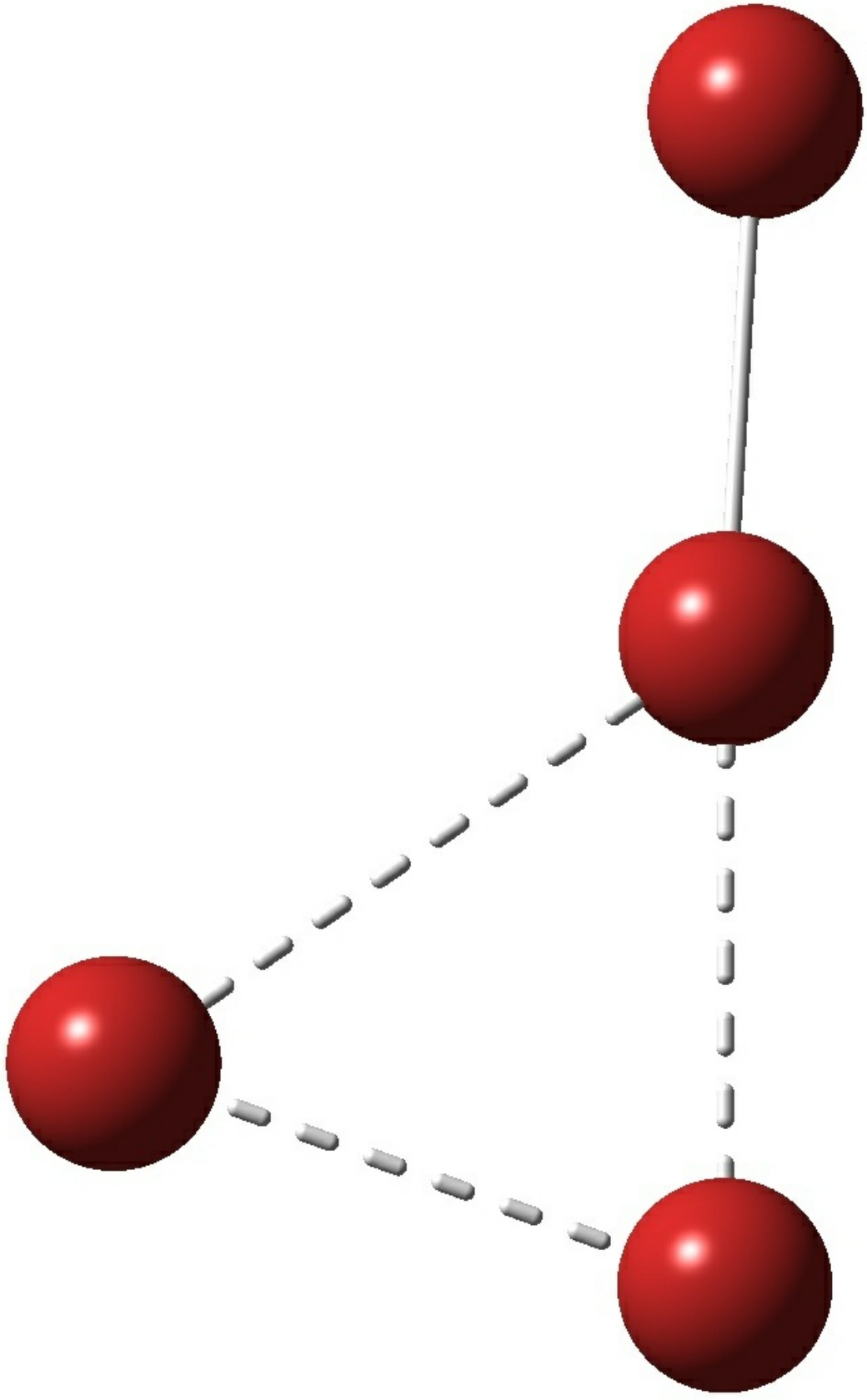
Allotropes are differing structural forms of the elements. The best known example is that of carbon, which comes as diamond and graphite, along with the relatively recently discovered fullerenes and now graphenes. Here I ponder whether any of the halogens can have allotropes.

Firstly, I am not aware of much discussion on the topic. But ClF3 is certainly well-known, and so it is trivial to suggest BrBr3, *i.e.* Br4 as an example of a halogen allotrope. Scifinder for example gives no literature hits on such a substance (either real or as a calculation; it is not always easy nowadays to tell which). So, is it stable? A B3LYP+D3/6-311++G(2d,2p) calculation reveals a free energy barrier of 17.2 kcal/mol preventing Br4 from dissociating to 2Br2.[1] The reaction however is rather exoenergic, and so to stand any chance of observing Br4, one would probably have to create it at a low temperature. But say -78° would probably be low enough to give it a long lifetime; perhaps even 0°.





So how to make it? This is pure speculation, but the red colour of bromine originates from (weak, symmetry forbidden) transitions, with energies calculated (for the 2Br2 complex) as 504, 492nm. Geometry optimisation of the first singlet excited state of 2Br2 produces the structure below, not that different from Br4.



At least from these relatively simple calculations, it does seem as if an allotrope of bromine might be detectable spectroscopically, if not actually isolated as a pure substance.

REFERENCES

1. Henry S Rzepa., "Br4", 2015. http://dx.doi.org/10.14469/ch/191228