A theoretical study of cesium borates compounds

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As part of a major nuclear accident, products resulting from the degradation of the control rods are likely to influence the transport of iodine in the reactor coolant system (RCS) of a pressurized water reactor (PWR). An international program PHEBUS-PF (replica at a 1/5000th scale of a PWR) was launched by the "Institut de Radioprotection et de Sûreté Nucléaire" (IRSN) to help the understanding of the phenomenology that can lead to releases of fission products to the environment in case of accident. A test PHEBUS-FP (FPT3) was performed in 2003 with control rods made of boron carbide (B_4C) and showed some unexpected results concerning iodine, with a high gaseous fraction at the break instead of a dominant aerosol fraction as observed in other tests. The boron may promote the gaseous iodine fraction at low temperature by preventing the CsI aerosol formation due to the possible formation of $Cs_xB_yO_z$ compounds (especially cesium metaborate $CsBO_2$). The behaviour of fission products in the RCS is modelled by the IRSN severe accident software ASTEC (accidental source term evaluation code). This modelling integrates some thermochemical equilibrium calculations whose data ($\Delta_f H°_{298K}$, $S°_{298K}$, $C_{p,T}$, $G°_{298K}$) have to be re-assessed in some cases resulting from large uncertainties. A valuable solution to estimate these data is to use the combination of quantum chemistry tools with statistical thermodynamics.

For the thermochemical study, structural parameters (geometries and vibrational frequencies) for CsB_yO_z, $Cs(B_yO_z)_2$ and $Cs_2(B_yO_z)_2$ compounds were determined using the B3LYP method associated with the cc-pVTZ and aug-cc-pVTZ basis sets for boron and oxygen atoms while the B3LYP/aug-cc-pVDZ level of theory was used to obtain the structural parameters in the case of the microsolvation of $CsBO_2$. In both cases, the caesium atom was described by the pseudopotential ECP46MDF developed by Lim et al.[1]. The potential energies were then computed using Dual-Level methodologies:

(i) for the thermochemistry of $Cs_xB_yO_z$: B3LYP/aug-cc-pVnZ//B3LYP/cc-pVTZ, B3LYP/aug-cc-pVnZ//B3LYP/aug-cc-pVTZ (n = T, Q, 5) levels of theory;

(ii) for the microsolvation: B3LYP/aug-cc-pVnZ//B3LYP/aug-cc-pVDZ (n = D, T, Q).

The results will be presented and compared with available literature data.

References:

[1] I.S. Lim, P. Schwerdtfeger, B. Metz, H. Stoll, J. Chem. Phys. 122, 104103 (2005)