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Binary and ternary Po-containing molecules relevant for LBE cooled reactors at operating temperature

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HIGHLIGHTS

- Ab initio methods assess the stability of Po-containing molecules above LBE.
- 13 plausible binary and ternary Po-containing molecules are considered.
- A fair compromise between accuracy and computational time is determined.

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ABSTRACT

Quantum-chemical calculations at several levels of theory were used to assess the stability at different temperatures of a set of 13 binary and ternary Po-containing molecules that could possibly be formed in an environment with lead, bismuth, oxygen and water. The conclusions are that especially PoPb, PbPoO and PoOH and to a lesser extent Po_2 and PoO are stable. These small molecules are therefore likely to be found near the Lead-Bismuth eutectic (LBE) coolant at operational temperatures in a heavy liquid metal cooled fission reactor. In contrast, Po_3 and PoBi are unlikely to be present under the assumed conditions. Several stability criteria, such as the dissociation into free atoms or into molecular fragments at realistic Po-concentrations or in the thermodynamic limit are discussed at different temperatures. The results obtained with a medium level of theory (Density Functional Theory, PBE0 with relativistic effective core potentials) show good qualitative correspondence with calculations performed at a much higher level of theory (Multi Reference Configuration Interaction, with spin–orbit coupling and scalar relativistic Hamiltonian).

1. Introduction

Lead-Bismuth eutectic (LBE) is under consideration as coolant for generation IV fission reactors, such as the planned MYRRHA reactor at SCK–CEN [1]. Neutron capture of ^{209}Bi present in the LBE results in a notable amount of radiotoxic ^{210}Po dispersed throughout the LBE volume. For safety reasons, it is important to know how this Po-contaminated LBE behaves, in operating conditions and accident scenarios.

For a reactor in operation, the liquid LBE serves as a natural container for the radiotoxic Po nuclei. Most of them will decay before they ever leave the coolant, especially at low temperatures. Some Po atoms, however, will eventually escape from the liquid, and will be present in the gas atmosphere above the coolant. The exact amount will depend to a large extent on the chemical properties of Po: if Po can form volatile molecules with elements commonly found in this environment, then more Po will be present in the gas atmosphere. The kind of molecules that can be formed will also determine which kind of filters are needed to capture them, in order to prevent release of Po outside the reactor system. For these reasons, we will examine in this work the stability of small molecules formed by Po at one hand and Pb, Bi, O and H at the other hand.

The aim of this paper is twofold: Firstly, we want to assess computationally the stability of a class of binary and ternary Po-containing molecules. Secondly, we want to examine which level of theory is sufficient to obtain reliable results. If one can resort to lower levels of theory and therefore to less demanding calculations, it will be possible to study molecules that are too complex to address with the high-level methods used in this work.

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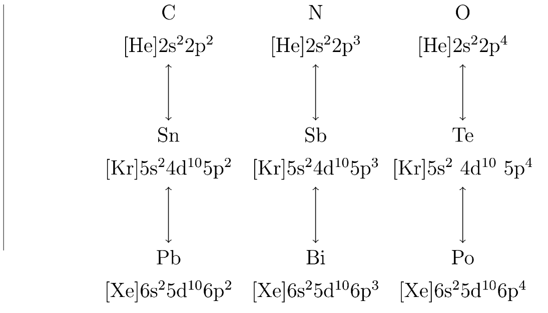
During the past decades, several experimental studies have examined the evaporation behavior of Po from LBE or from similar heavy liquid metals [2–6]. Abakumov suggests not only atomic Po, but also diatomic Po-containing molecules will appear in polonium vapor [7]. The vapor over pure polonium is expected to consist of Po_2 molecules [8], whereas in a polonium-poor environment – as in the case of LBE – different compounds could be formed. Studies of Feuerstein et al. [9] and Gromov et al. [10] report on Po evaporation in the form of lead-polonide (PoPb) or elementary Po. This observation was supported by the observation of PbTe and Te evaporation from Tellurium in LBE. As observed by Moyer, low evaporation rates of Polonium from a Bismuth–Polonium mixture suggests PoBi is evaporated rather than elementary Po [11,9]. Also Polonium hydride (H_2Po) is assumed to be produced in the interaction with water and is therefore expected in the LBE cover gas [12–15,6]. However, its presence is questionable on basis of its thermodynamical instability [2,16,17]. More recently, the thermochromatography study of Maugeri et al. [18] tentatively assigns observed experimental signals to PoO, PoOH and PoO_2. The latter molecule was previously reported by Abakumov [7], although it is not assumed to be stable in the cover gas above the LBE [2].

In most of the experimental studies mentioned above, no direct determination of the kind of Po-containing molecule was made. Instead, a plausible candidate molecule was found to be consistent with the experimental observations. To some extent, this approach contains an (unavoidable) degree of subjectivity. Therefore, in the present work we will take the complementary approach. We consider a relatively large set of postulated binary and ternary Po-containing molecules, inspired by well-known light homologues (see Fig. 1). The partner elements in these molecules were selected based on their prevalence near LBE and on their likeliness to interact. In particular we have included the interaction with the LBE, water and the most reactive elements in air. Binary and ternary Tellurium molecules found throughout literature are listed in Fig. 1 as well. They confirm that the postulated set of Po-molecules is meaningful [19–21]. Although Po could possibly form PoO_3, homologous to TeO_3 [20], this system lies beyond the scope of this work focussing on binary and ternary molecules. First principles calculations are subsequently used to assess which of the postulated molecules are stable at all. The most stable ones are those that should be primordially considered in the analysis of experiments. Most theoretical studies on heavy elements focus on fundamental aspects, using a variety of computationally very demanding methods [22–24]. The challenges within this respect are twofold: Firstly the introduction of relativistic effects is expected to be important. Secondly, sufficient electron correlations should be incorporated in the applied method to predict accurate dissociation energies.



OH	→	TeH	→	PoH	H_2O	→	H_2Te	→	PoH_2
CO	→	TeSn,TePb	→	PoBi	CO_2	→	SCTe	→	Po_2Pb , PoPbO
NO	→	TeSb	→	PoPb	NO_2	→		→	Po_2Bi , PoBiO
O_2	→	TeO	→	PoO	O_3	→	TeO_2	→	Po_3 , Po_2O, PoO_2
O_2	→	Te_2	→	Po_2					

Fig. 1. (top) The chemical equivalence between second row elements (C, N and O), fifth row elements (Sn, Sb and Te) and sixth row elements (Pb, Bi and Po) is shown here by the electron configuration of each element; (bottom) a set of 13 Po-containing molecules that can be formed by analogy to familiar molecules formed by light chemical elements and/or Te-containing binary and ternary molecules.

2. Theoretical framework and computational details

2.1. Literature review

The most simple approach to describe relativistic effects in molecules with heavy elements is to use a set of pre-constructed relativistic effective core potentials (RECP). This approach reduces the all-electron quantum chemical problem to only the valence electrons and replaces the presence of the core electrons by an effective potential, in which the major relativistic effects are implicitly incorporated [25]. This constitutes a serious approximation, but it has been used frequently for handling similar complexes [26,27] and is unavoidable when considering extended systems. Several variants have been proposed [28] and in some of them spin–orbit effects have been neglected [29].

A more accurate approach is to include scalar relativistic effects variationally with a Douglas–Kroll–Hess (DKH) [30,31] or Zeroth Order Regular Approximation (ZORA) Hamiltonian [32–34]. Originally the ZORA approach was developed in a two-component approach, but a spin-free adaption is more frequently used [33]. In Ref. [34] the two-component ZORA approach is compared with the full four component Dirac solution with discrepancies acceptable for the current purpose (*i.e.*, <O(0.05) Å for the internuclear distance and <O(0.03) eV for the dissociation energy). It can be concluded that the ZORA is sufficient to describe valence properties even for superheavy elements – *i.e.*, 7p atoms. In the present work, we will only consider atoms containing up to 6p electrons for which relativistic effects are even smaller, affirming the ZORA Hamiltonian to be valid in this situation.

Next to the scalar relativistic effects, the spin–orbit coupling is expected to be non-negligible. Different approaches are available to include this interaction. The fully variational treatment assumes a two-component solution for which the spin–orbit operator is solved iteratively and is therefore part of the Fock operator acting on a two-component spinor. Most papers use a perturbative treatment however, in which the spin–orbit operator expectation value is calculated for the ground state or the spin–orbit operator is diagonalized in a basis set constructed by the ground state and several excited states (quasi degenerate perturbation theory, QDPT). Those expectation values and matrix elements can themselves be calculated in multiple ways, *e.g.* using nuclear screening [35], using an effective potential [36], the atomic-mean-field (AMFI) [37] or the related spin–orbit mean field (SOMF) methods [38].

The four component method, used as a reference to benchmark the ZORA approach in Ref. [34], is the most complete description since it starts from the Dirac equation. The method also treats positrons, but is complex and computationally quite expensive, especially when a high level wavefunction approach is also envisaged. Recently, several papers have used these methods [22,39]: Pershina et al. [22,40,41] applies an in-house relativistic Density Functional Theory (DFT) method within the noncollinear spin-polarized formalism [42]. Their objective is to calculate systems including atoms which are situated one row lower in the periodic table, or even beyond [43]. Comparison of dissociation energies and bond distances of M_2 molecules, where M are elements up to the 7th row, revealed a different trend for the 7th row elements compared to their lighter homologues, caused by a dominant spin–orbit coupling. Since Polonium is a 6th row element, spin–

orbit effects are important but probably not dominant. In our study we will not go beyond the 6th row and a perturbative treatment of spin–orbit coupling is justified [44].

2.2. Computational details

Two types of calculations were performed in this work: one at a medium level and one at a high level of theory. All of them were carried out using the ORCA program [45]. The medium level calculations are based on the DFT method treating the relativistic effects with RECP [46] (see Section 2.1). This method is compared to accurate high level all-electron calculations which rely on scalar relativistic effects through the ZORA Hamiltonian and using Multireference Configuration Interaction (MRCI) as the solver. Spin–orbit coupling was treated perturbatively in the latter method. Both methods will be described hereafter in more detail.

In the medium-level RECP method, only valence electrons are treated quantum-mechanically (see Section 2.1). This method parameterizes the most important relativistic effects into an effective core potential and enables the use of available non-relativistic quantum chemistry methods. This valence-only approximation can be justified since the core electrons are unlikely to participate in the chemical bond and the reduced complexity allows a more accurate treatment of the valence electrons. Also from a computational point of view, this approach will be unavoidable for follow-up studies that examine, for instance, more complex containing molecules. The calculations are performed at the Density Functional Theory (DFT) level using the PBE0 [47,48] functional and a cc-pVTZ [49–51] basis set for the valence electrons of Pb, Bi and Po. The same basis set was used for all electrons of O and H. All molecules were optimized at this level of theory. As commonly known, such a single reference method is however inadequate to derive a full dissociation profile [52]. Therefore the dissociation energy ΔE_{el} was calculated as the difference between the energy of the optimized structure and the sum of the energies of their fragments. A consequence of this approach is that it is not possible to use a ZORA Hamiltonian to describe scalar-relativistic effects: the original formulation does not yield gauge invariance [32]. This artefact can be solved by including a system dependent model potential in the Hamiltonian. This solution causes the ZORA Hamiltonian to change when another system is considered. In particular, the model potential for a small molecule is different to the one for its fragments. A simple subtraction of energy is therefore inconsistent and the ZORA Hamiltonian is not size-extensive [33]. These problems do not occur for the non-relativistic Hamiltonian in combination with the RECP.

Secondly, all-electron calculations are performed using the ZORA Hamiltonian [32,33] to take into account the scalar relativistic effects. For these calculations the ZORA-adapted TZVP [53,54] basis set was used. The calculations were performed with Multireference Configuration Interaction (MRCI) following a Complete Active Space Self Consistent Field (CASSCF) calculation. The CAS consists of all 6p orbitals for Pb, Bi and Po, 2p orbitals for O and 1s, 2s and 2p orbitals for H. This high level of theory allows to accurately determine the dissociation energy curve for binary molecules and thus the use of a model-potential based ZORA Hamiltonian poses no problem. From the energy curve, the dissociation energy ΔE_{el} and bond distance R_e can be fitted to a Morse potential.

$$M(R) = \Delta E_{el}(1 - \exp(-a(R - R_e)))^2 \quad (1)$$

To reduce the computational cost, the ternary molecules were not optimized at this high level of theory but their DFT geometries were used. Due to the lack of size-extensibility in a CI approach, the energy of the dissociated molecule is calculated for the three fragments at sufficiently large distance ($\approx$10 Å).

The spin–orbit and spin–spin interactions were treated at the quasi-degenerate perturbation theory (QDPT) level [55], both for the equilibrium geometry and the dissociated molecule. The spin–spin interaction will not be reported in what follows, since its contribution is negligibly small.

The influence of temperature is investigated for each system by comparing the (Gibbs) free energy at 0 K, near the melting point of LBE ($\approx$400 K) and near the maximum operation temperature ($\approx$750 K). The frequency calculations, required to obtain the free energies (G) for the systems under study, are all calculated at the medium-level of theory (DFT with PBE0 functional).

The total internal energy U is given by

$$U = E_{el} + E_{ZPE} + E_{vib} + E_{rot} + E_{trans} \quad (2)$$

and the free energy at temperature T (G_T) by

$$G_T = U + k_B T - T(S_{el} + S_{vib} + S_{rot} + S_{trans}) \quad (3)$$

both containing electronic (*el*), vibrational (*vib*), rotational (*rot*) and translational (*trans*) contributions to the energy (E) and the entropy (S). Additionally, also the zero temperature vibrational energy (*ZPE*) is present in the internal energy expression. At 0 K the free energy (G_{0K}) corresponds to the internal energy U without vibrational, rotational and translational contributions, which are thermal effects, but with ZPE-contribution. Only differences in (free) energies between two geometrical configurations will be reported, which will be indicated by Δ (*e.g.* ΔG).

3. Results and discussion

In order to select a plausible set of binary and ternary molecules for Po in an environment with LBE, air and water, we take advantage of the fact that Pb, Bi and Po are isoelectronic to Sn, Sb and Te and to the lighter elements C, N and O. We consider all known binary and ternary molecules where at least one oxygen atom (to be replaced by Po) is combined with carbon or nitrogen (to be replaced by Pb or Bi) and hydrogen or other oxygen atoms. As can be seen from Fig. 1, this approach leads to a set of which several of the Te-versions are effectively reported in the literature. For Po, it leads to the set of 5 binary and 8 ternary Po-containing molecules that is listed in Fig. 1. This set includes all binary and ternary molecules that have been proposed based on experimental work (see Section 1).

Firstly we focus on binary molecules for which the dissociation energy was calculated at both a medium level of theory (DFT with RECP) and high level of theory (CASSCF – see Table 1 for details – with subsequently MRCI and spin–orbit corrections with all-electron ZORA basis set). This allows to benchmark the medium level of theory which then will be subsequently used for the ternary species, for which the high level becomes computationally very expensive.

3.1. Binary molecules

The calculated dissociation energies ΔE_{el} and corresponding bond distances R_e for the binary molecules are given in Table 2.

Table 1
Active space of binary molecules, defined through the number of active electrons (n_{el}) and active orbitals (n_{orb}). The last column gives information about the considered spin-multiplicity and the number of roots for this spin-state is given between brackets.

Molecule	n_{el}	n_{orb}	2S + 1 (n_{roots})
PoH	5	8	2(2)
PoO	8	6	1(3), 3(3)
PoPb	6	6	1(1), 3(9)
PoBi	7	6	2(4), 4(5)
Po_2	8	6	1(3), 3(3)

Table 2
Equilibrium distance (R_e) and dissociation energy (ΔE_{el}) for the binary molecules with different spin multiplicity. Four different results are included: DFT calculations were preformed with the PBE0 functional, RECP and a cc-pVTZ basis set. Secondly, all-electron calculations with a ZORA-adapted TZVP basis set are performed, subsequently with CASSCF, MRCI and a SOC correction on the MRCI results. For this, a ZORA-adapted TZVP basis set was used.

	2S + 1	DFT (PBE0, RECP)		CASSCF		MRCI		MRCI + SOC	Literature	
		R_e (Å)	ΔE_{el} (eV)	R_e (Å)	ΔE_{el} (eV)	R_e (Å)	ΔE_{el} (eV)	ΔE_{el} (eV)	ΔE_{el} (eV) (exp.)	ΔE_{el} (eV) (calc.)
PoH	2	1.7480	2.6760	1.7572	2.3327	1.7531	2.5213	2.8098		2.25[b], 2.428[c]
PoO	1	1.9220	2.3382	1.9806	2.1388	1.9729	2.4681			
	3	1.9208	3.4328	2.0079	1.6748	1.9470	3.0609	3.0704	2.88[a]	2.92[b]
PoPb	1	2.6720	3.5395	2.9690	1.5985	2.6989	3.4050	3.4112		
	3	2.9312	2.1120	3.0025	1.2358	2.9311	2.0074			
PoBi	2	2.6950	2.2638	3.0305	0.6304	2.7227	2.0647	1.5742		
	4	2.8593	0.2534	2.7607	1.3989	2.9536	1.1676			
Po_2	1	2.7171	1.8855	2.7511	1.8514	2.7590	1.9820			2.15[d], 1.938[a]
	3	2.7210	2.6702	2.8299	1.1763	2.7329	2.3680	2.5635		

[a] Ref. [56] (exp.).
[b] Ref. [57] at mixed DFT/CCSD(T) level of theory (calc.).
[c] Ref. [28] using MCQDPT (calc.).
[d] Ref. [22] using 4-component DFT (calc.).

For completeness all investigated spin states are reported for DFT, CASSCF and MRCI calculations, while the spin–orbit corrections were only performed on the ground state. Due to the limited availability of experimental reference data, also computational results from literature are included.

Table 2 lists first the DFT results with RECP (some correlation, indirect effective spin–orbit coupling), secondly the CASSCF calculations (static correlation, no spin–orbit interaction) and finally the MRCI calculations (static plus dynamic correlation, done with and without spin–orbit interaction). The spin–spin contribution was calculated with MRCI and turned out to be negligible (results not reported).

Overall, the distances are not very much influenced by the computational method, in agreement with other theoretical work. For the dissociation energy ΔE_{el}, the inclusion of dynamic correlation is essential as clearly demonstrated by the comparison between CASSCF and MRCI calculations. On the other hand, the effect due to the inclusion of spin–orbit coupling is rather unpredictable: in most cases it causes a more tight binding, with widely varying size. In contrast, for PoBi, the spin–orbit interaction leads to less binding which is exceptional within this small set of molecules. A much larger dataset would, however, be needed to draw more decisive conclusions. Fortunately, the use of relativistic effective core potentials performs quite well, as shown in the correlation plot in Fig. 2. The computational cost can therefore drastically be reduced. In general, DFT appears to overbind the binary molecules slightly compared to the high-level reference calculations. The strength of all bonds is, however, of the same order of magnitude for the medium and the high-level method (see Fig. 2).

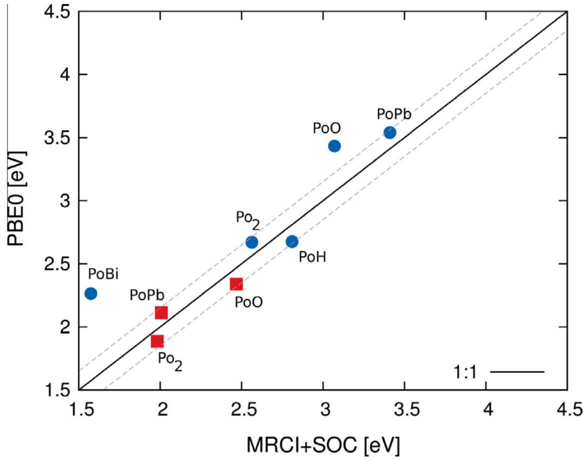


Fig. 2. Correlation between MRCI and DFT dissociation energies with respect to free atoms (considering only ΔE_{el}) for the testset of binary molecules. The blue circles indicate the most stable spin-states, the red squares correspond to higher-energy spin states (also included in Table 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3 documents the impact of the ZPE and temperature on the dissociation energy. For the binary molecules the ZPE is a rather small contribution, while temperature effects are more pronounced. PoPb and PoO are clearly the most stable molecules, at all temperatures, followed by PoH and Po_2. In realistic reactor conditions, however, the abundance of Po is that low that molecules with more than one Po are unlikely to appear. In the binary series, PoBi turns out to have the lowest dissociation free energy at all temperatures and hence it can be considered to be the molecule which is most unlikely to be found near the LBE. These conclusions are consistent with the identification of PoPb as a stable molecule which evaporates from both LBE and Pb–Li eutectic [58,9,4] and with the recent hypothesis of PoO being formed near the LBE [18]. In literature, PoH was not yet considered to be present near the LBE. This candidate is however nearly as stable as other binary molecules, confirmed by both DFT and literature data [56,57,28,22], also at higher temperatures.

A different approach to discuss the stability of the diatomic molecules, is to consider dissociation reactions of the Po-molecules into elemental atoms and reactive molecules present in the LBE cover gas (i.e. O_2 and H_2). The results are listed in Table 4. From these free energy differences (ΔG_T), again PoPb is found to be by

Table 3
Dissociation energy (ΔE_{el}) and free dissociation energy at 0 (ΔG_{0K}), 400 (ΔG_{400K}) and 750 K (ΔG_{750K}) for binary and ternary systems considered in this work. Positive values mean the considered molecule will form a bond.

	ΔE_{el} (eV)	ΔG_{0K} (eV)	ΔG_{400K} (eV)	ΔG_{750K} (eV)
PoH	2.6760	2.5310	2.2145	1.8778
PoO	3.4328	3.3850	3.0306	2.6720
PoPb	3.5395	3.5276	3.1462	2.7827
PoBi	2.2638	2.2525	1.8868	1.5374
Po_2	2.6702	2.6583	2.3160	1.9868
PoH_2	5.5259	5.1846	4.5171	3.8051
PoO_2	6.3159	6.1988	5.3900	4.5917
PoOH	7.1322	6.7743	6.0528	5.3049
PbPoO	6.5430	6.4731	5.6647	4.8498
$PbPo_2$	5.7948	5.7702	4.9731	4.2351
BiPoO	5.1798	5.1157	4.3542	3.6263
$BiPo_2$	4.7382	4.2932	4.9842	2.8227
Po_3	4.0231	4.0009	3.2221	2.5006
Po_3	4.0347	4.0120	3.2749	2.5910

Table 4
Possible dissociation reactions within our subset of binary Po-containing molecules (supplemented with the elemental atoms and O_2 and H_2). All values rely on DFT results which allows to use the difference in free energy $\Delta G_T = G(products) - G(reactants)$.

Reaction	ΔG_{0K} (eV)	ΔG_{400K} (eV)	ΔG_{750K} (eV)
$PoPb \rightarrow \frac{1}{2}Po_2 + Pb$	2.1984	1.9882	1.7893
$PoBi \rightarrow \frac{1}{2}Po_2 + Bi$	0.9234	0.7288	0.5441
$PoO \rightarrow \frac{1}{2}Po_2 + \frac{1}{2}O_2$	−0.5890	−0.5829	−0.5819
$PoH \rightarrow \frac{1}{2}Po_2 + \frac{1}{2}H_2$	−0.9252	−0.8839	−0.8621

far the most stable molecule over all temperatures considered. The formation of PoO and PoH is energetically unfavorable, according to this stability criterion. The energy difference is however not extremely large and combined with the low probability to have Po_2 at these small Po concentrations, the presence of PoO and PoH cannot be ruled out.

Hereafter, the comparison between the DFT and MRCI results are discussed in more detail for every binary molecule in particular. In Fig. 3 the dissociation profiles – calculated at the MRCI level of theory – for the different molecules are plotted.

3.1.1. PoH

Polonium hydride has a double degenerate ground state and has one unpaired electron. All studied methods predict the atoms to bind with this spin multiplicity (*i.e.* 2S + 1 = 2). It is clear from comparison between the CASSCF and MRCI calculations that inclusion of electron correlation and spin–orbit coupling causes the bond to be stronger (see Table 2). With a dissociation energy ΔE_{el} of 2.8 eV, the most accurate method (MRCI + SOC, see Fig. 3a) gives a result that is larger than the ones of all other methods. The dissociation energy calculated from DFT lies somewhere in between the MRCI and MRCI + SOC value and relatively close to the most accurate prediction within the set of methods considered here.

3.1.2. PoO

For polonium monoxide, multiple spin states are considered. The MRCI calculations show the ground state to be non-degenerate and can be labeled by the $^3\Sigma$ molecular term symbol in absence of SOC. The first excited state is the double degenerate $^1\Delta$ state (see Fig. 3b), followed by $^1\Sigma$ and $^3\Pi$ states, all forming stable bonds. In this work the main interest goes to the ground state, which has a dissociation energy of 3.07 eV, in rather close agreement with experimental data and data from references [56,57]. MRCI slightly overestimates the dissociation energy, with respect to experiment and literature. The influence of spin–orbit coupling is minor, which is remarkable for this high spin system. CASSCF goes completely wrong, predicting a dissociation energy for the triplet which is more than 1 eV less bound and putting the singlet state forward as the most stable. DFT is more reliable: it predicts the correct ground state at the right position, but overestimates the binding energy (3.43 eV).

3.1.3. PoPb

The most stable binary molecule is the polonium–lead complex with a binding energy of approximately 3.4 eV (MRCI) or 3.53 eV (DFT). The ground state is the singlet $^1\Sigma$ state. Spin–orbit coupling again has little influence on the stability of the ground state (see Fig. 3c). Due to the high abundance of Pb in the system, this is a very likely candidate to form near the LBE surface.

For PoPb we can draw the same conclusion as for PoO with respect to the spin–orbit coupling: it makes the ground state (here a singlet) a little bit more bound, while DFT slightly overestimates and CASSCF completely fails in reproducing the correct binding profile.

3.1.4. PoBi

Both DFT and MRCI calculations predict a spin-doublet character for the Polonium–bismuth ground state. In contrast to all other molecules, the dissociation energy is lowered by the introduction of spin–orbit coupling (see Fig. 3d). The DFT dissociation energy follows this trend with slightly tighter bound molecules compared to the MRCI results, in correspondence with the spin–orbit corrected MRCI results for all other molecules. Therefore, the lowering of dissociation energy due to spin–orbit interaction is not found with DFT, probably because this effect was not anticipated in the construction of the RECP used for these calculations.

3.1.5. Po_2

With the same number of valence electrons as oxygen, it is not surprising that dipolonium is found in a triplet ground state $^3\Sigma$ as predicted by DFT and MRCI methods (see Fig. 3e). In literature only the dissociation energy for the singlet state is reported, in very close agreement with the MRCI result obtained in this work. We found however that the triplet state is more bound, even at higher temperatures.

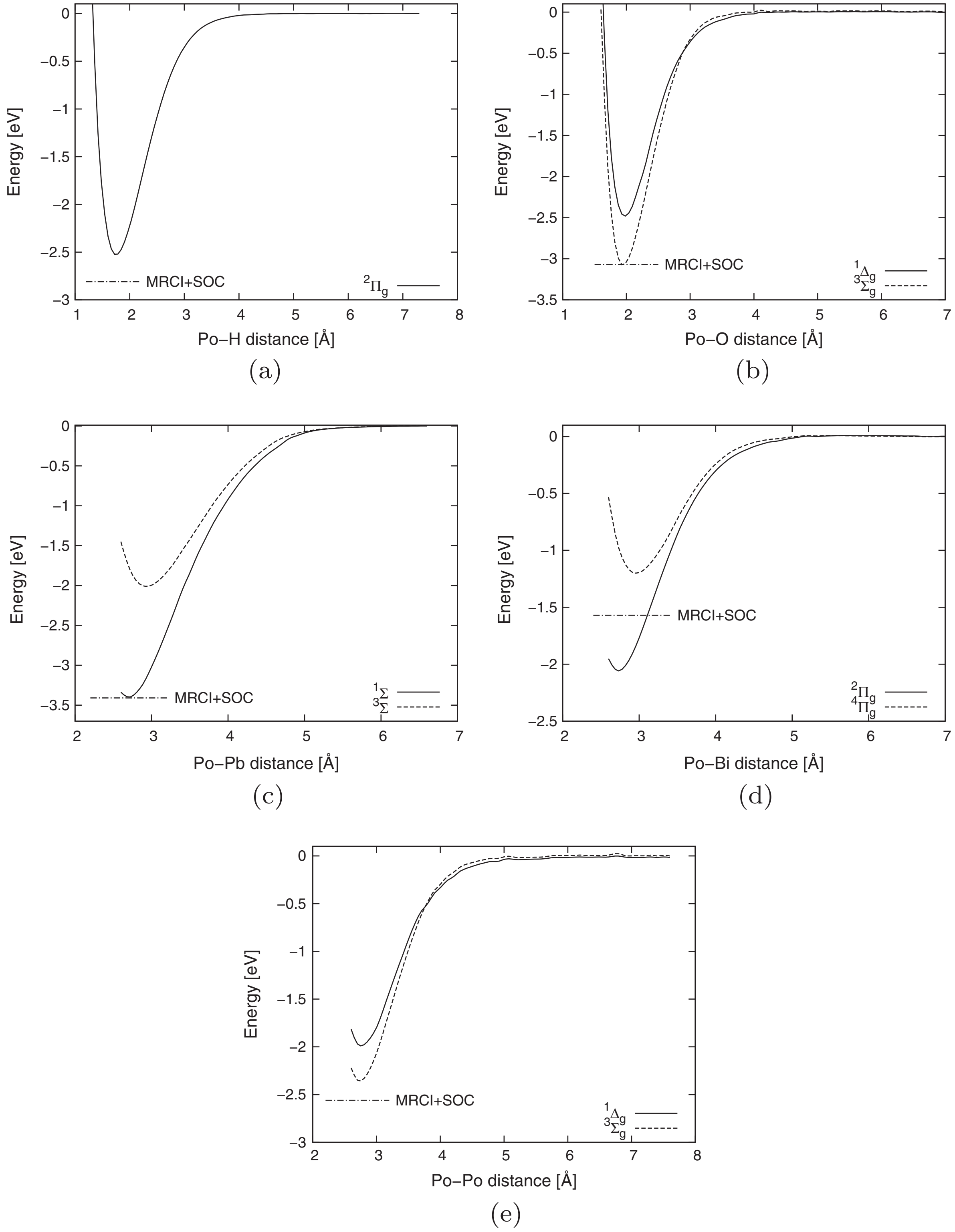
3.2. Ternary molecules

Secondly, ternary molecules were considered. Their geometry determination and dissociation energy prediction was done at the medium level of theory (*i.e.* DFT with PBE0 functional and RECP). For a few manageable cases, the energy was calculated at higher levels of theory as well. In contrast to their light-element homologues, there is no a priori knowledge about their geometry. Since high energy barriers between different conformers might not be overcome during a geometry optimization, up to six relevant starting geometries were considered. Among those were also geometries beyond the principle of equivalence with light homologues. Below, the results are presented for the most stable configurations. In the right hand side of Table 5 two internuclear distances (A–B and B–C) and the angle ($A\hat{B}C$) are listed for all ternary molecules. The sequence of atoms (A–B–C) is chosen in such a way that the A–B and B–C distances are the smallest ones and the angle $A\hat{B}C$ is the largest (see Fig. 4).

When describing the stability of these molecules, multiple reference states can be considered. First, the free atoms can be chosen as a reference, similar to the binary molecules described above. These dissociation energies are listed in Table 5 (at 0 K) and in Table 3 (at higher temperatures). Secondly, all possible reactions can be considered that transform the ternary molecule into the sum of free atoms and/or binary molecules (*e.g.* $2BiPoO \leftrightarrow 2Bi + Po_2 + O_2$). We limit ourselves to reactions that have at their right-hand side any of the binary Po-containing molecules in Fig. 1, extended with the free atoms and O_2 and H_2. Depending on whether the left-hand side or right-hand side of the reaction has the lowest energy, the ternary molecule is either stable or unstable in the thermodynamic limit. In typical reactor conditions of Po evaporating from the LBE, some of these reactions are statistically unlikely to happen due to the small amount of Po in the atmosphere. Therefore, a third stability criterion is considered: the dissociation free energy of a ternary molecule with respect to one binary molecule and one atom.

3.2.1. Stability with respect to free atoms

Regarding the dissociation energy with respect to the free atoms, the results are listed in Tables 3 and 5. Table 5 contains the available dissociation energies ΔE_{el} for MRCI + SOC, compared to the DFT results. Only few systems could be verified using the demanding MRCI + SOC calculations, due to computational limitations or convergence issues. From those limited cases, the discrepancy between the MRCI + SOC and DFT results is larger than for the



(a) (b) (c) (d) (e)

Fig. 3. Dissociation curves of the different binary molecules considered in this work: (a) PoH, (b) PoO, (c) PoPb, (d) PoBi and (e) Po_2. All curves are calculated with MRCI and multiple spin states are considered. The influence of the spin–orbit interaction is systematically indicated by a full horizontal line.

binary cases, with the MRCI + SOC dissociation energy being smaller than the DFT dissociation energy. One plausible explanation is that for MRCI + SOC no geometry optimization was performed, which does not rule out the existence of small geometry changes with possible large energy differences. Allowing full geometry optimizations at a MRCI + SOC level would necessarily reduce the discrepancy with DFT. There is no indication in Table 5 that DFT leads to qualitatively wrong results, but actual values of the dissociation energies from DFT should be used with some care.

The influence of the ZPE is—not surprisingly—larger for the ternary systems compared to the binary, especially when more light elements are present in the system. It is, however, not a dominant factor. The temperature gives rise to a non-negligible contribution to the free energy. The conclusion about stability of the molecules

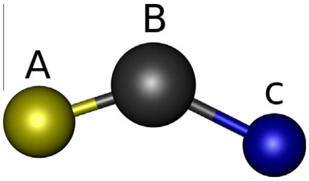


Fig. 4. A dummy ternary molecule to illustrate the values in Table 5. In cases where two equivalent atoms are present in the system, the two outer elements A and C are chosen identical. For all others, the labeling of the atoms is chosen such that A–B and B–C represent the smallest internuclear distances (with A–B the smallest of the two) and θ_{ABC} represents the largest angle.

is however unaltered. At all evaluated temperatures, the binding energy is sufficiently large to conclude that all considered molecules can be formed. As far as this stability criterion is concerned, these molecules will be present near the LBE.

3.2.2. Stability in the thermodynamical limit

As it is impossible to examine all reactions that involve these ternary molecules, we have limited ourselves to the subset of dissociation reactions that result into any of the binary molecules from Section 3.1, and/or the free Pb, Bi or Po atoms, O_2 and H_2. These reactions are considered at 0 K, 400 K (melting point of LBE) and 750 K (highest operation conditions of MYRRHA). The molecules PbPoO, PoOH, BiPoO, Po_2Pb and Po_2Bi turn out to be stable against all examined dissociation reactions (see Table 6). Po_2O, PoH_2 and PoO_2, on the other hand, decay at thermodynamical equilibrium into smaller fragments. It must be stressed that this does not mean that a molecule as PoO_2 cannot exist in typical reactor conditions: as Po is rare anyway, the chance that two PoO_2 molecules meet and react to form Po_2 and 2 O_2 is small. There are indeed experimental claims for the existence of PoO_2 in similar conditions [7,18]. Similarly, PoH_2 was also found experimentally, although it was not expected to be thermodynamically stable [2,16,17], which is consistent with our results. Although Po_3 has a positive free energy balance at zero Kelvin, it is found not to be stable at operational temperatures.

3.2.3. Stability with respect to fragments

In Table 7, the free energy difference between an isolated ternary Po-containing molecule and a binary molecule combined with a free atom is listed. Several reaction paths have been examined, all listed in Table 7. In each case, we considered the most stable Po-containing binary and an atom, as indicated. All these free energy differences are quite large at 0 K, most of them far beyond 1 eV (to be compared with positive reaction energies that can be below 0.1 eV in Table 6) and few around this value (e.g. PoH_2, PoO_2 and Po_3).

At higher temperatures however, the free energies are systematically reduced, showing that the stability of especially PoO_2 becomes very small. The molecule can be present anyway, depending on the transition state of this reaction. This lies beyond the scope of this work. Similar, but less dramatic, also the dissociation free energy of PoH_2, BiPoO, $BiPo_2$ and Po_3 become smaller than 1 eV, however still positive. At the operation conditions, they still are to be assumed plausible molecules. The molecules containing Po and Pb are typically much more stable, even at the highest temperatures. Also the hydration of Po is quite strong, which was investigated more in detail by Ayala et al. [26].

Table 6
Possible reactions considered for the formation or dissociation of the ternary Po molecules. For positive reaction free energies, the reactants are most stable, for negative reaction free energies the products are formed in the thermodynamical limit. $\Delta G_T = G(products) - G(reactants)$.

Reaction	ΔG_{0K} (eV)	ΔG_{400K} (eV)	ΔG_{750K} (eV)
$2PbPoO \leftrightarrow 2Pb + Po_2 + O_2$	2.50	2.05	1.59
$2PoOH \leftrightarrow Po_2 + 2OH$	1.15	0.96	0.75
$2BiPoO \leftrightarrow Po_2 + 2Bi + O_2$	1.14	0.74	0.37
$2Po_2Pb \leftrightarrow 2PoPb + 2Po_2$	0.91	0.67	0.46
$Po_2Bi \leftrightarrow Po_2 + Bi$	0.06	0.04	0.03
$2Po_3 \leftrightarrow 3Po_2$	0.05	−0.40	−0.80
$2Po_2O \leftrightarrow 2Po_2 + O_2$	−0.35	−0.61	−0.85
$2PoH_2 \leftrightarrow Po_2 + 2H_2$	−0.40	−0.53	−0.68
$2PoO_2 \leftrightarrow Po_2 + 2O_2$	−0.42	−0.68	−0.92

Table 7
Free energy differences between ternary molecules with respect to the fragments. Calculations performed with RECP at a DFT level of theory. The dissociation free energy ΔG at temperature T is defined as $\Delta G_T = G(products) - G(reactants)$.

Reaction	ΔG_{0K} (eV)	ΔG_{400K} (eV)	ΔG_{750K} (eV)
$PoH_2 \leftrightarrow PoH; H$	2.6536	2.3027	1.9274
$PoH_2 \leftrightarrow Po; H_2$	0.9304	0.6364	0.3122
$PoO_2 \leftrightarrow PoO; O$	2.8138	2.3595	1.9197
$PoO_2 \leftrightarrow Po; O_2$	0.9092	0.7000	0.0707
$PoOH \leftrightarrow PoO; H$	3.3893	3.0222	2.6329
$PoOH \leftrightarrow Po; OH$	2.4802	2.1148	1.7396
$PbPoO \leftrightarrow PbPo; O$	2.9455	2.5185	2.0671
$PbPoO \leftrightarrow PoO; Pb$	3.0881	2.6341	2.1777
$PbPo_2 \leftrightarrow PbPo; Po$	2.2426	1.8269	1.4525
$PbPo_2 \leftrightarrow Po_2; Pb$	3.1119	2.6571	2.2483
$BiPoO \leftrightarrow PoO; Bi$	1.7307	1.3236	0.9543
$BiPoO \leftrightarrow PoBi; O$	2.8632	2.4674	2.0889
$BiPo_2 \leftrightarrow BiPo; Po$	2.0407	1.6431	1.2852
$BiPo_2 \leftrightarrow Po_2; Bi$	1.6349	1.2138	0.8359
$Po_3 \leftrightarrow Po_2; Po$	1.3426	0.9061	0.5139
Po_3[a] $\leftrightarrow Po_2; Po$	1.3537	0.9588	0.6040

[a] The dissociation free energy for the triplet state.

Although some ternary molecules are expected to dissociate into smaller fragments at temperatures slightly higher than 750 K, for the operation conditions in the MYRRHA reactor, all free energies considered in this work are still positive. This implies that

Table 5
Dissociation energy of ternary molecules with respect to the free atoms at the DFT, CASSCF, MRCI and MRCI + SOC levels of theory and structural information of ternary molecules, optimized by RECP with DFT. For Po_3 the values for both triplet (1) and singlet (2) states are given because both dissociation energies are very close to each other while the geometrical parameters show significant differences.

	2S + 1	DFT D_e (eV)	CASSCF D_e (eV)	MRCI D_e (eV)	MRCI + SOC D_e (eV)	A–B–C	R_{AB} (Å)	R_{BC} (Å)	θ_{ABC} (°)
PoH_2	1	5.5259	3.9267	5.2736	4.7846	H–Po–H	1.7459	1.7459	89.47
PoO_2	1	6.3159	3.9485	5.5158	5.0456	O–Po–O	1.8933	1.8937	107.11
PoOH	2	7.1322				Po–O–H	2.0644	0.9610	106.89
PbPoO	1	6.5430	4.4129	6.1493		Po–O–Pb	2.1689	2.1012	82.93
$PbPo_2$	1	5.7948				Po–Pb–Po	2.8944	2.8938	61.68
BiPoO	2	5.1798	3.2400	4.3351		Po–Bi–O	2.8975	1.9101	99.87
$BiPo_2$	2	4.7382				Po–Bi–Po	2.8948	2.8970	60.92
Po_3(1)	1	4.0231				Po–Po–Po	2.8133	2.8126	82.57
Po_3(2)	3	4.0347				Po–Po–Po	2.7549	2.7549	113.39

an isolated Po-containing ternary molecule that does not meet another (rare) ternary molecule, is unlikely to spontaneously decay into a Po-containing binary.

In typical reactor conditions with very small Po-concentrations, these ternaries are therefore stable with respect to binaries.

4. Conclusion

In this work we calculated the dissociation (free) energies of small Polonium-containing molecules to investigate their possible formation in a generation IV fission reactor, for which LBE is used as a coolant. The dissociation energies were calculated at a high level of theory – MRCI with inclusion of scalar relativistic effects and SOC – as well as at a more approximative medium level of theory – DFT with RECP. A hybrid functional (PBE0) was used for the DFT calculations. Although some disagreement between both levels of theory is found – indicating the crucial role of relativistic effects in these systems – rather similar trends are observed. Therefore we can conclude that a DFT approach in which only the valence electrons are variationally treated due to the use of RECPs, is sufficient a level of theory to study the behavior of Po-containing molecules.

From all the molecules examined in this work, especially PoPb, PbPoO and PoOH are found to be stable according to all considered stability criteria and at all considered temperatures. PoO and PoO_2 are very stable against dissociation into free atoms but in the thermodynamical limit, a more stable set of molecules is found. The dissociation of PoO_2 into atomic polonium and oxygen becomes stable only slightly above 750 K, which is however the maximum temperature to be reached in operational conditions of the MYRRHA reactor. Po_2 can also be considered as a stable molecule. In contrast, Po_3 and PoBi have small dissociation energies, becoming even smaller at higher temperatures. Despite the prediction of molecules with only Po and light elements being unstable in the thermodynamic limit, the considered reactions require presence of multiple Po atoms very near to each other, a situation which is unlikely under operation conditions of LBE.

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