

How Elementary Mercury Reacts in the Presence of Halogen Radicals and/or Halogen Anions: A DFT Investigation

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Abstract: Reactions of elementary mercury in the gas phase (GEM) have been investigated at the DFT level in the presence of halogen radicals and/or halogen anions. In the presence of radicals, the formation of HgX_3^{\cdot} and HgX_4^{2-} is predicted to be favourable. Moreover, in the presence of anions, the free-radical liberation is enhanced from these two species allowing the presence of halogen free radicals even without the presence of light radiation. This enhancement is associated with the formation of HgX_3^- , which is predicted to be the most stable species. In

solution, redox chemistry can occur and transform GEM in the presence of X_2 . The redox potentials of the couples HgX_2/Hg for $\text{X}=\text{Cl}$, Br and I were calculated to be 0.52, 0.48 and 0.04 V, respectively. This study gives new opportunities to elucidate the environmental chemistry of Hg in the polar regions. In these areas GEM has a unique and fast

reactivity due to a combination of factors such as the polar sunrise, the presence of halogenated radicals, snow and ice surfaces and cold temperatures. This reactivity, known as atmospheric mercury depletion events (AMDEs), leads to the deposition of significant amounts of Hg^{2+} in these regions. The reaction pathways of AMDEs are as yet unknown and the DFT approach may contribute to their elucidation and to the proposal of new mechanisms. Additionally, this study introduces hypotheses concerning the reactivity of GEM inside snowpacks.

Keywords: density functional calculations • environmental chemistry • mercury • radical reactions • redox chemistry

Introduction

Mercury is a toxic metal emitted into the environment by both natural and anthropogenic sources. The major chemical form in the atmosphere is gaseous elementary mercury (GEM or Hg^0) with global background concentrations at remote sites of 1.5–1.7 ng m^{-3} in the northern hemisphere and of 1.1–1.3 ng m^{-3} in the southern hemisphere.^[1] The atmos-

pheric lifetime of GEM is generally evaluated to be around one year and is thus sufficient to allow for long-range transport. Deposition of GEM onto environmental surfaces occurs following its oxidation by oxidants such as ozone and hydroxyl radicals.^[2] Recently, halogen radicals, especially bromine and bromine oxides have been suspected to be the main chemical oxidants in polar atmospheres in spring when atmospheric mercury depletion events (AMDEs) occur.^[3,4] The halogen radicals are thought to be generated by means of a series of photochemical and heterogeneous reactions involving bromide from sea salt.^[5] During AMDEs, Hg^0 is rapidly transformed into water-soluble and reactive species of Hg (gaseous Hg^{II} complexes and/or Hg^{II} bound to particles) leading to a massive deposition of divalent Hg onto environmental surfaces such as snowpacks, sea ice and open ocean. Consequently, an increase of Hg^{II} content in the snow has been reported in many Arctic sites following AMDEs.^[6,7] The deposition of Hg in the snow is not an irreversible process and the snowpack can behave like a source of Hg. On many occasions, a part of the deposited Hg is re-emitted back into the atmosphere after the reduction of Hg^{II} complexes in the snow, which is likely to be light-initiated.^[8,9] Interestingly, several observations throughout the Arctic show

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that snowpacks are also a sink for atmospheric mercury.^[10–12] The reaction pathways, the reactants that are involved and the medium for the reaction—in the interstitial air of the snow, in the snow grain volume, at the snow/air interface in the liquidlike layer of water—are as yet undefined.

The role of halogen species in the transformation of mercury has deserved a lot of attention during the last few years.^[13,14] However, this field of research is largely unexplored because many uncertainties remain regarding the pathways and products of Hg⁰ oxidation. Because analytical methods are not adapted to the detection of halogen radicals and byproducts of reactions in the field, many studies are based on computing approaches.^[15–17] For instance, Calvert and Lindberg^[15] suggested the possibility of Hg-containing products, such as HgO, HgBr₂, BrHgOBr and BrOHgOBr. Goodsite et al.^[17] proposed some mechanisms based on the initial recombination of Hg⁰ with Br, followed by the addition of a second radical (Br, I or OH) in competition with thermal dissociation of HgBr.

Theoretical investigation is a good way of studying the reactivity of elementary mercury in the gas phase in the presence of either halogen radicals or halogen anions. Calculations on mercury systems are rather scarce in the literature and mainly deal with the possibility of using d electrons to obtain the Hg^{IV} oxidation state.^[18–22] However, Tossel^[23] reported a theoretical investigation of the thermal formation of Hg^{II} complexes in the presence of various radicals. Balabanov et al.^[24–26] also reported dynamical studies on the collision of mercury atoms with halogen molecules. Theoretical methods, and in particular DFT methods, have proven in the past their ability in predicting the reactivity of metallic complexes.^[27] Thus, we first present in this contribution a study on the reaction of elementary mercury with a series of halogen radicals from Cl to I in the gas phase. In particular, the optimal number of ligands will be determined, thus indicating that elementary mercury can coordinate more than two radicals. This can induce important environmental effects because such complexes, with more than two radicals coordinated, could act as a source of halogen radicals without solar light in deep snowpacks. Following this, the possibility of a redox reaction between elementary mercury and halogen anions will be discussed by determining theoretically the redox potential for the HgX₂/Hg couples. The knowledge of these potentials allows us to predict the formation or the destruction of elementary mercury in the presence of anions in solution. Finally, competing coordination between radicals and anions will be presented. It will be shown that the trigonal HgX₃[•] complexes are found to be the most stable rather than the tetrahedral HgX₄^{2•}. This is explained by the lower repulsion between the electrons on the ligand and the d electrons in the former case than in the latter. These theoretical approaches could have important implications in terms of the environmental chemistry of mercury, both in the atmosphere and in snowpacks. These points will be examined in the last part of this contribution.

Computational Methods

Mercury^[28] and all the halogen atoms^[29] were treated with a Stuttgart–Dresden pseudopotential in combination with their adapted basis set, augmented by a set of polarisation functions (f for Hg and d for halogens).^[30,31] Calculations were carried out at the DFT level using the hybrid functional B3PW91.^[32,33] Geometry optimisations were carried out without any symmetry restrictions; the nature of the extremum (minimum) was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 03^[34] suite of programs, and the free Gibbs energy values were obtained within the harmonic approximation at 298.15 K.

Results and Discussion

Reaction of elementary mercury with halogen radicals: Reactions between GEM (labelled Hg in the following) and two, three and four halogen radicals (Cl, Br and I) have been computed. A picture of the representative structures is given in Figure 1. As can be seen from Figure 1, it has not only been possible to obtain a stable structure for HgX₂, as expected, but also for HgX₃[•] and HgX₄^{2•}. Even though HgX₂ is known to be a very stable structure,^[23,34] to the best of our knowledge neither of the other two structures has been reported in the literature. A recent combined experimental/theoretical study by Andrews and Kaupp et al.^[22] reported the existence in the gas phase of tetravalent mercury species, such as HgF₄. However, to the best of our knowledge, the existence of either radical or diradical mercury species has never been mentioned in the literature. HgX₂ has a standard linear structure, in agreement with the use of s and p orbitals, with two equivalent Hg–X distances (Table 1).

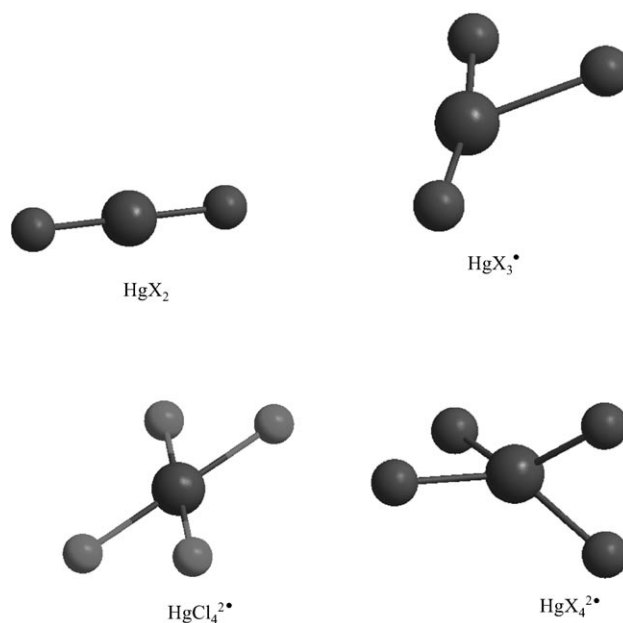


Figure 1. Representative structures of the complexes formed by reaction between GEM and two (HgX₂), three (HgX₃[•]) or four (HgX₄^{2•}) halogen radicals.

Table 1. Hg–X distances [Å] in the HgX₂, HgX₃[·] and HgX₄^{2·} complexes.

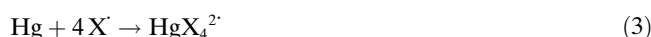
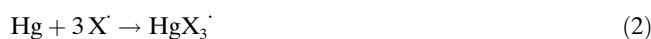
	Hg–X ₁	Hg–X ₂	Hg–X ₃	Hg–X ₄
HgCl ₂	2.28	2.28	–	–
HgCl ₃ [·]	2.28	2.28	2.91	–
HgCl ₄ ^{2·}	2.35	2.35	2.88	2.88
HgBr ₂	2.42	2.42	–	–
HgBr ₃ [·]	2.43	2.43	2.95	–
HgBr ₄ ^{2·}	2.65	2.65	2.65	2.65
HgI ₂	2.63	2.63	–	–
HgI ₃ [·]	2.64	2.76	2.96	–
HgI ₄ ^{2·}	2.84	2.84	2.84	2.84

The structure for HgX₃[·] (doublet spin state) is very interesting because rather than a standard trigonal or “T-shape” structure a “Y-shape” structure is obtained. This distortion can be explained by the fact that the complex exhibits two different types of ligand: two “classical” ligands like in HgX₂ and a radical X[·]. This is clearly marked by the Hg–X distances (Table 1): two are found to be identical and one is much longer (however, the distance is smaller than the sum of the van der Waals radii, thus indicating an interaction). The angle X–Hg–X (using the two similar ligands) is found to be close to 180°, which indicates that the structure can be described as a slightly distorted HgX₂ complex interacting with X[·]. The analysis of the spin density further supports this since an electron is lying on the extra halogen ligand. It should also be noted (Figure 1) that two different geometries were obtained for HgX₄^{2·} (triplet spin state) depending on X. For Cl, a distorted square-planar arrangement around Hg was obtained, whereas a distorted tetrahedron was obtained for Br and I; it should however be noted that the two structures only differ by a rotation of 90° of a formal X₂^{2·} moiety. These geometries differ from a perfect tetrahedron more than would have been expected. This can simply be explained by the fact that one is dealing with open-shell systems and thus the standard molecular orbital view is maybe not sufficient. Moreover, as in the monoradical case, two types of halogen ligand can be observed, as found by looking at the Hg–X distances. This is further confirmed by analysing the spin density and thus, two ligands are “classical” and the other two are radicals interacting with the metal centre.

The obtained complexes exhibit some interesting geometrical features. To find out more, the coordination energy in the gas phase was also determined. In Table 2, the free energy of the following reactions [Eqs. (1)–(3)] has been collected:

Table 2. Gibbs free energy [kcal mol^{–1}] for the reactions defined in Equations (1)–(3).

	Cl	Br	I
HgX ₂	–82.3	–66.7	–51.9
HgX ₃ [·]	–87.4	–72.3	–59.0
HgX ₄ ^{2·}	–87.4	–74.0	–61.0



As expected and in agreement with the values in the literature,^[23] the coordination of two radicals to the mercury centre is highly favourable in the gas phase for all halogens. Interestingly, the coordination of the third and fourth halogen radical is also found to be thermodynamically favourable, leading to stable structures.

Moreover, it appears that these two extra coordinations (leading to HgX₃[·] and HgX₄^{2·}) are calculated to be only slightly exergonic with respect to the two first ones (formation of HgX₂) so that these radical species could act as a halogen free-radical source. The environmental implication of this will be examined at the end of this report.

Reaction of elementary mercury with halogen anions: The presence of a quasi-liquid layer in the snowpack makes the reaction in solution possible, as mentioned in the introduction. Thus, other possible chemical processes of GEM oxidation without light irradiation have been studied by using theoretical methods. In this context, a particular interest has been devoted to oxydo-reduction processes that could occur in solution. Thus, reactions involving the HgX₂/Hg and X₂/X[–] redox couples have been studied. These reactions can be envisioned since Foster^[36] reported the formation of Br₂ mainly by oxidation of Br[–] by O₃. To validate the possibility of redox process between the two couples, it has been necessary to evaluate the redox potential of the HgX₂/Hg couple. The half-redox equation [Eq. (4)] can be written as follows:



By combining this equation with the one obtained for the X₂/X[–] couple (X₂ + 2e[–] → 2X[–]), it is possible to obtain the following global reaction (that would simply be an oxidation of GEM by X₂) [Eq. (5)]:



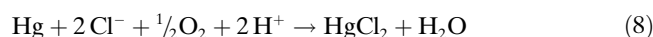
According to the Nernst law, the Gibbs free energy of this reaction can be written according to the redox potentials and the two couples as follows [Eq. (6)]:

$$\Delta G = -2F(E_{\text{X}_2/\text{X}^-}^0 - E_{\text{HgX}_2/\text{Hg}}^0) \quad (6)$$

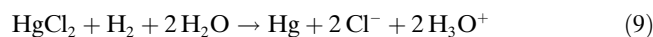
By calculating the Gibbs free energy of the reaction and knowing the redox potential of the couple X₂/X[–], it is thus possible to determine the redox potential of the couple HgX₂/Hg according to Equation (7):

$$E_{\text{HgX}_2/\text{Hg}}^0 = E_{\text{X}_2/\text{X}}^0 + \frac{\Delta G}{2F} \quad (7)$$

Analysing this equation clearly indicates that if the global reaction is calculated to be exergonic, the redox potential of the HgX_2/Hg couple will be lower than that of the couple X_2/X^- and GEM will be oxidised. If the global reaction is endergonic, the redox potential of the HgX_2/Hg couple will be greater than that of the couple X_2/X^- and GEM will be formed. The Gibbs free energy of reaction for the three halogen atoms was computed at the DFT level and found to be exergonic in all cases: $-38.7 \text{ kcal mol}^{-1}$ for Cl, $-29.9 \text{ kcal mol}^{-1}$ for Br and $-26.7 \text{ kcal mol}^{-1}$ for I. This global reaction has been calculated to be exergonic by $29.9 \text{ kcal mol}^{-1}$ in agreement with a facile reaction. Thus, in the presence of X_2 , GEM can be oxidised to form HgX_2 by an oxydo-reduction process. It is thus possible to determine the redox potentials in the three cases, namely, HgCl_2/Hg (0.52 V), HgBr_2/Hg (0.48 V) and HgI_2/Hg (0.04 V), by knowing the redox potential of Cl_2/Cl^- (1.36 V), Br_2/Br^- (1.13 V) and I_2/I^- (0.62 V). Thus, as an example, in presence of the couple $\text{O}_2/\text{H}_2\text{O}$ (1.229 V), GEM should be formed according to Equation (8):



with an expected Gibbs free energy of reaction of $\Delta G = -2F(E_{\text{O}_2/\text{H}_2\text{O}}^0 - E_{\text{HgX}_2/\text{Hg}}^0)$. This reaction will be exergonic; the lower Gibbs free energy of reaction is expected for Cl ($-35.9 \text{ kcal mol}^{-1}$). On the other hand, in the presence of $\text{H}_3\text{O}^+/\text{H}_2$ (0.00 V), GEM should also be formed by reduction of HgX_2 according to Equation (9):



with an expected Gibbs free energy of reaction of $\Delta G = -2F(E_{\text{HgX}_2/\text{Hg}}^0 - E_{\text{H}_3\text{O}^+/\text{H}_2}^0)$. This reaction will be exergonic; the lower Gibbs free energy of reaction is expected for I ($-1.8 \text{ kcal mol}^{-1}$). Thus, according to the composition of the medium, formation or destruction of GEM can occur through redox chemistry.

Reaction of elementary mercury at the gas/solution interface: The possibility of GEM reacting with both halogen radicals and halogen anions at an interface between the gas and liquid phases has been investigated. We have restricted ourselves to the coordination of halogen anions to HgX_2 , formed by the addition of two halogen radicals to GEM. Thus, the formation of HgX_3^- and HgX_4^{2-} has been investigated and will be compared to the corresponding radical species $\text{HgX}_3\cdot$ and $\text{HgX}_4^{2\cdot}$ [see Eqs. (1)–(3)]. A picture of the representative structures of HgX_3^- and HgX_4^{2-} is given in Figure 2. As can be seen, the obtained geometries for both systems are those expected because a perfect trigonal pyramid and a tetrahedron are found. All of the ligands in each of these systems are of the same type and the Hg–X distances in each are the same. Interestingly, these distances are exactly the same as those obtained for the “classical”

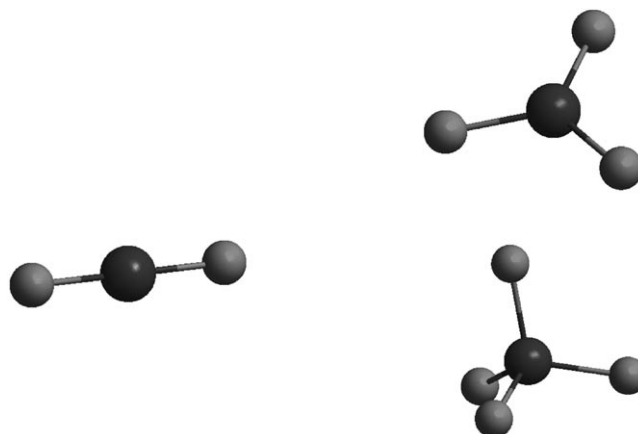
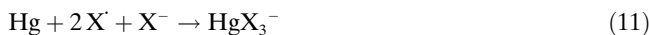


Figure 2. Representative structures of the complexes formed by reaction between GEM and two (HgX_2), three (HgX_3^-) or four (HgX_4^{2-}) halogen anions.

ligand in the radical structures (see Table 1). In Table 3, the free energy of the following reactions [Eqs. (10)–(12)] has been collected:

Table 3. Gibbs free energy [kcal mol^{-1}] for the reactions defined in Equations (10)–(12).

	Cl	Br	I
HgX_2	-82.3	-66.7	-51.9
HgX_3^-	-122.7	-105.1	-88.2
HgX_4^{2-}	-72.1	-54.7	-38.8

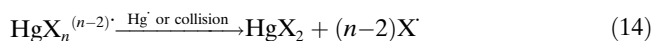
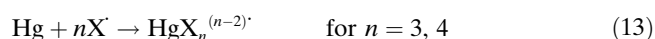


As expected and in agreement with the values in the literature,^[35] the formation of HgX_3^- is highly favourable in the gas phase for all halogens. On the other hand, the formation of the tetrahedral HgX_4^{2-} is predicted to be unfavourable. This can simply be explained by the repulsion between the ten d electrons of the mercury and the valence electrons of the four halogen ligands (eight electrons). This repulsion is greater for mercury than for other atoms of Group 12, since by relativistic effects the 5d shell is close in energy to the 6s and 6p shells used for making the bonds with the ligands.

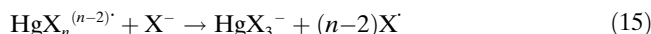
By comparing the formation energies of the radical and anionic forms of HgX_3 it appears that the anionic structure is more stable than the radical one. The stability of such a complex was already reported in the literature.^[35] On the other hand, it is noteworthy that the radical form of HgX_4 is more likely than its anionic formulation mainly due to the repulsion between the d electrons and the valence electron of the anions. Thus, the predicted most stable form in the solution of mercury, in the presence of halogen anions, is

HgX_3^- . The latter could either be formed by a direct addition of X^- to HgX_2 or by the substitution of one(two) radical(s) by an X^- on HgX_3^{\cdot} ($\text{HgX}_4^{2\cdot}$). For example, the formation of HgCl_3^- from HgCl_3^{\cdot} (with the liberation of a Cl radical) is predicted to be exergonic by $-122.3 \text{ kcal mol}^{-1}$ (the same energy is predicted for the formation of HgCl_3^- and the liberation of two Cl radicals from $\text{HgCl}_4^{2\cdot}$). Thus, in solution the coordination of a chlorine anion can induce the halogen free-radical liberation from the radical mercury complexes.

Environmental consequences for the chemistry of mercury in the polar atmospheres and snowpacks: In polar atmospheres, GEM can be rapidly oxidised during atmospheric depletion events by means of halogen radical chemistry.^[3] Kinetic studies show that Br radicals could be the only candidate for the fast oxidation of GEM.^[14] Bromine radicals are produced from the photolysis of Br_2 , which can be generated by heterogeneous processes occurring at the surface of atmospheric aerosols, snow grains between bromine anions and ozone.^[36] To date, the products of GEM oxidation in the environment have not been identified, mainly because of the lack of suitable analytical methods.^[7] Goodsite et al.^[17] postulated that the reaction between GEM and bromine radicals can lead to the formation of gaseous HgBr_2 via the formation of a first intermediate, HgBr . Interestingly we found that the coordination with three and four halogen radicals gave even more stable structures. Thus the production of $\text{HgBr}_3^{\cdot}/\text{HgCl}_3^{\cdot}$ and/or $\text{HgBr}_4^{2\cdot}/\text{HgCl}_4^{2\cdot}$ could also account for the removal of GEM during AMDEs. These byproducts give an interesting perspective because they can release halogen free radicals. For instance, a collision with another Hg atom or a water vapour molecule is sufficient to induce such a release. In the absence of light the release of halogen free radicals is thus possible in theory. If we consider that $\text{HgBr}_3^{\cdot}/\text{HgCl}_3^{\cdot}$ and/or $\text{HgBr}_4^{2\cdot}/\text{HgCl}_4^{2\cdot}$ are formed during AMDEs, it implies that an interaction with atmospheric particles or their deposition onto snow and ice surfaces is likely to induce the release of new free radicals. This pathway can lead to a catalytic cycle of Hg^0 destruction such as that shown below [Eqs. (13) and (14)]:



We previously showed that the formation of HgX_3^- is favourable in solution. Hence if a gas/solution interface is present—such as leads and polynyas (areas of open water in sea ice) or open ocean waters—we can predict that following the reaction shown in Equation (13), the reaction in Equation (15) may give a rapid source of one or two radicals available for GEM oxidation:



Thus the presence of open water, for example, or another air/water interface could be a way to promote the depletion of atmospheric GEM as shown in Figure 3.

For convenience, in Figure 3, the reactions only involve Br atoms. One should note that similar pathways can be

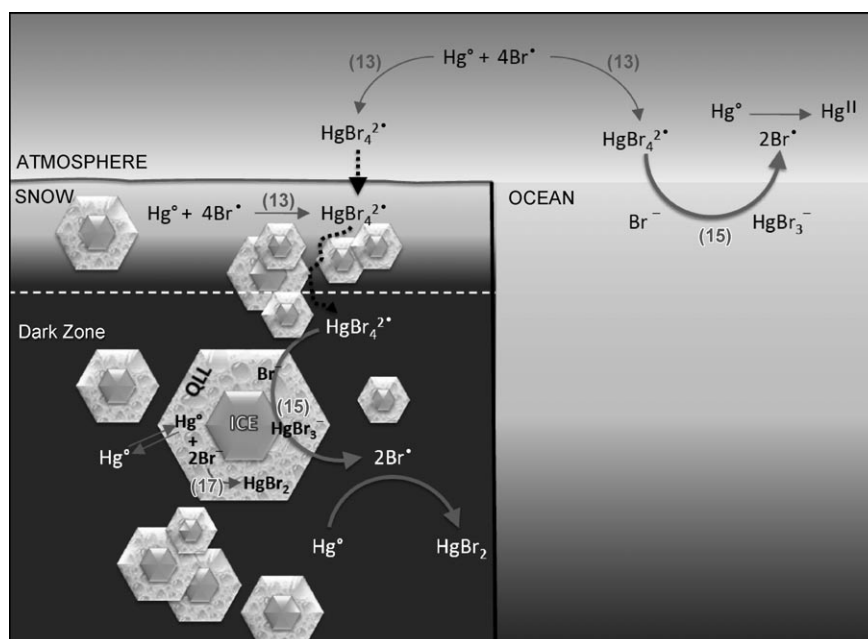


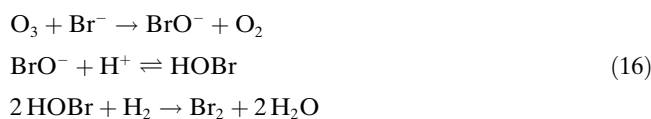
Figure 3. A schematic view of some oxidation pathways of gaseous elemental mercury (GEM, Hg^0) in polar regions, based on the reactions defined in Equations (13), (15) and (17) ($n=4$).

written with chlorine atoms. Bromine atoms can be produced through the photolysis of Br_2 (see, for instance, ref. [36]). On the right side, we show a mechanism that could promote and accelerate AMDEs in the presence of open seawater. The product of Equation (13) is involved in Equation (15) at the seawater/air interface. The resulting product Br^{\cdot} is likely to oxidise GEM giving a supplementary pathway for AMDEs. On the left side, we show how GEM can be oxidised in the air of a snowpack in the dark. The reaction in Equation (13) is likely to occur both in the atmosphere and in the first layer of the snow. Bromine radicals can be produced in the snowpack as well. This mechanism can be thus possible without any AMDEs if a source of Br^{\cdot}

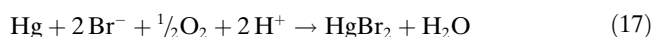
is active. HgBr_4^{2-} can be transported in deeper layers of the snow where light is no longer available. Then the reaction in Equation (15) may occur at the air/liquid interface, that is, at the quasi-liquid layer (QLL)/air interface. A reaction [Eq. (17); see below] is also possible in the QLL. Both pathways lead to the oxidation of GEM in the air of the snow.

The previous reactions are interesting from the perspective of elucidating the measurements of GEM obtained in the interstitial air of snowpacks. On many occasions, the production or the destruction of GEM has been observed in the interstitial air of seasonal snowpacks or snowpacks above glaciers or ice caps.^[8,11,37–39] The production of GEM in the first layers of snow was not surprising because many divalent Hg complexes are known to be sensitive to natural sunlight.^[35] However, the depletion of GEM in the air of snow in the deepest layer in the dark or at night is more unexpected. As illustrated in Figure 3, this theoretical study gives some new tips and shows that GEM can be oxidised in the dark by the release of a halogen radical from radical complexes of Hg such as HgBr_3^{\cdot} . Additionally, the quasi-liquid layer, which surrounds the snow grains and where many chemical and photochemical reactions are believed to be accelerated (e.g., see ref. [40]), can provide a source of anions at a liquid/gas interface for the liberation of a free radical from the radical mercury complexes. This unexpected source of radicals will be able to oxidise GEM rapidly in the air of the snowpack and in the dark. Finally, redox chemistry proves that GEM can be oxidised through dark reactions. Oum et al.^[41] and Foster et al.^[36] reported the existence of a mechanism explaining the destruction of ozone

and the production of Br_2 in the first layers of snow together with a decrease of bromine anions with depth. The suggested mechanism occurring at the air/ice interface is the following [Eq. (16)]:



Following our study, an additional step can be added for the destruction of GEM in solution (in the QLL) [Eq. (17)]:



These mechanisms can be applied to field experiments conducted at high latitude and coastal snowpacks. Similarly to what has been reported with O_3 by Foster et al.^[36] or Albert et al.^[42] in the snowpack of Alert (82°N, Canada), Ferrari et al.^[11] found a rapid decrease of GEM with depth in the interstitial air of the snowpack of Station Nord (81°N, Greenland, Denmark). In addition, they observed lower Hg^{2+} concentrations in the surface snow than at deeper levels. The data obtained for these two different Arctic sites and at the same period of the year (after the polar sunrise) are compiled in Figure 4.

Under these conditions of light and in that particular snowpack at Station Nord, GEM may be potentially oxidised at all depths in the snowpack by means of Equation (17) or by the release of radicals by Equation (15) (see

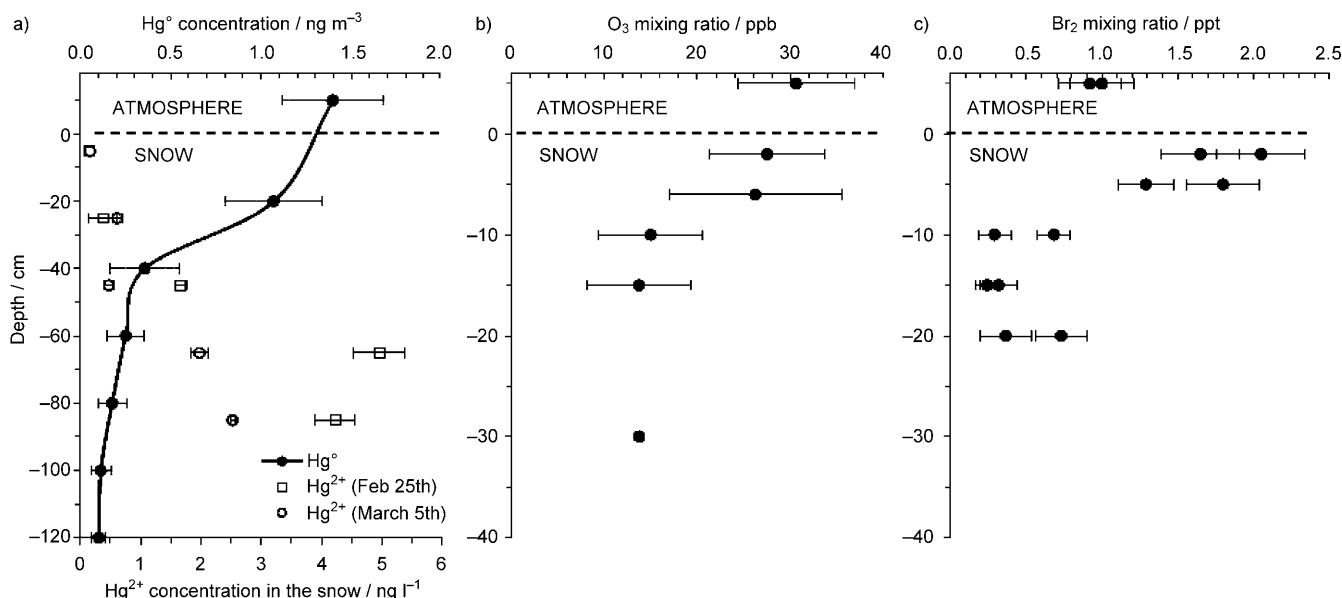


Figure 4. Profiles of GEM, ozone and Br_2 measured in the air of Arctic snowpacks after polar sunrise. a) Mean GEM measurements in the atmosphere and in the air of snow obtained at Station Nord, Greenland (81°N) from February 25th to March 5th. Two sets of measurements of Hg^{2+} concentration in the snow are also reported. Measurements at 5 cm below the surface are below the detection limit of the analytical system (0.16 ng l⁻¹). These data are available in ref. [11]. b) Ozone mixing ratio in the atmosphere (35 cm above the surface) and in the air of snow obtained at Alert, Canada (82°N) from February 29th to March 9th during twilight conditions. The same decreasing trend can be observed before (10–28 February) and after (15–30 March) this period. Data are extracted from ref. [42]. c) Br_2 mixing ratio in the atmosphere (25 cm above the snow surface) and in the air of snow obtained at Alert, Canada (82°N) on March 3rd. Data are extracted from ref. [36].

Figure 3). However, since light is only available at the top layer,^[43] reduction and photoreduction of Hg complexes such as the one formed in Equation (17) tend to compensate or dominate the oxidation process. As a result, the concentration of GEM in the top layers is close to atmospheric level or even higher. As the light decreases exponentially with depth,^[43] oxidation may be the only process that occurs at greater depths. Nevertheless, we are aware that this explanation is incomplete because we do not take into account all redox reactions and do not consider the kinetics. To go further, the whole chemical composition of the snow with respect to anionic and cationic species, the role of organic matter and the full speciation of Hg should be investigated both in the field and in theory.

Conclusion

In this article, reactions between halogen radicals (and/or halogen anions) and GEM have been investigated by using DFT methods. It has been possible to show that in the presence of halogen radicals, $\text{HgX}_3^{\cdot-}$ and HgX_4^{2-} complexes were predicted to be stable and energetically more favourable than HgX_2 . However, the difference in energy between the complexes and HgX_2 is rather small leading to a relatively facile liberation of free radicals. Moreover, it has been shown that in the presence of an anion the free-radical liberation from the two radical mercury complexes ($\text{HgX}_3^{\cdot-}$ and HgX_4^{2-}) is favoured to form HgX_3^- , which is predicted to be the most stable species. Thus, this source of halogen free radicals can allow the depletion of GEM without the presence of light.

Another alternative for the creation or destruction of GEM without light is that a redox reaction can occur in solution. We have been able to calculate and to predict the redox potentials of the couples HgX_2/Hg for $\text{X} = \text{Cl}, \text{Br}$ and I . These redox potentials are found to be 0.52 V for Cl, 0.48 V for Br and 0.04 V for I. Thus, based on the knowledge of the composition of snowpacks, it is possible to predict either the formation or the destruction of GEM. These redox potentials are therefore an interesting tool to predict the possible reactions in solution, even though they do not deal with the kinetics.

This original approach of Hg chemistry in the environment has broad implications for our understanding of reactions occurring in polar regions. It appears that the oxidation of Hg is a poorly understood process. The question of halogen radical sources suggests that AMDEs are not clearly defined and that the mechanisms suggested above could play a role in the atmospheric depletion of Hg. The fact that snowpacks can be a sink for mercury with internal reactions has to be elucidated. However, this hypothesis becomes more and more reasonable and confirmed by multiple field observations as well as by computational studies.

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