Gas-Phase Photolysis of Hg(I) Radical Species: A New Atmospheric Mercury Reduction Process

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Supporting Information

ABSTRACT: The efficient gas-phase photoreduction of Hg(II) has recently been shown to change mercury cycling significantly in the atmosphere and its deposition to the Earth’s surface. However, the photolysis of key Hg(I) species within that cycle is currently not considered. Here we present ultraviolet–visible absorption spectra and cross-sections of HgCl, HgBr, HgI, and HgOH radicals, computed by high-level quantum-chemical methods, and show for the first time that gas-phase Hg(I) photoreduction can occur at time scales that eventually would influence the mercury chemistry in the atmosphere. These results provide new fundamental understanding of the photobehavior of Hg(I) radicals and show that the photolysis of HgBr increases atmospheric mercury lifetime, contributing to its global distribution in a significant way.

Mercury is a developmental neurotoxin that is transported in the atmosphere in elemental and oxidized forms. Elemental mercury is characterized by low chemical reactivity and it remains long enough in the atmosphere (∼1 year) to become a global contaminant, albeit in very low concentration (1–2 ng m⁻³)³. Anthropogenic emissions to the atmosphere are essentially from burning coal and it remains long enough in the atmosphere (∼1 year) to become a global contaminant, albeit in very low concentration (1–2 ng m⁻³)³.

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Maximum activity second-order perturbation theory, (MS-
CASPT2\textsuperscript{21–24} as implemented in MOLCAS,\textsuperscript{25} to predict absorption spectra and cross-sections by well-established computational techniques,\textsuperscript{26,27} used before for spectra calculation of a series of Hg(II) compounds.\textsuperscript{6} Finally, a kinetic model for the atmospheric redox (photo)chemistry of the Hg(0), Hg(I), and Hg(II) species was built based on the computed data (see Supporting Information (SI)).

The relevant molecular orbitals of the HgX (X = Cl, Br, I, OH) radicals are shown in Figure 1, while Tables S1–S3 present geometrical and thermochemical data calculated for these species, both in the ground and first bound electronically excited-state, together with previous available experimental and computed values.

The PEC diagrams of these radical species were calculated including spin-orbit (SO) coupling. Those corresponding to HgBr, as a function of the internuclear distance, and HgOH as a function of the Hg–OH coordinate are shown in Figure 2. The remaining PECs are displayed in Figures S1 and S2. The electronic-state nomenclature designated in previous spectroscopic analysis\textsuperscript{28–30} is retained here. For the HgX (X = Cl, Br, I) monohalides, A and B denote the lowest-lying excited spin free (SF) states $^{2}\Pi$ and $^{2}\Sigma$ and C and D is used for each of the SO states (with $\Omega = 1/2$ and 3/2) related to the high-energy $^{2}\Pi$ SF state. The ground and excited electronic states of all the HgX radicals computed here contain mixtures of ionic and covalent configurations, as was noted by previous calculations of the Cl and Br mercury monohalides.\textsuperscript{12}

The calculated bond-dissociation energy ($D_0$) of the weakly bound $X \Sigma^+$ ground-state of the monohalides (Tables S1 and S2) decreases rapidly from $\approx 100$ (Cl) to $\approx 30$ (I) kJ mol$^{-1}$, in very good agreement with existing experimental data. The agreement extends also to equilibrium geometry and harmonic frequencies. In the case of the isoelectronic HgOH radical, the ground-state binding energy of the Hg–OH bond is even lower, and would compromise the stability of this radical. Inclusion of SO effects does not affect the $D_0$ values, since the electronic ground-state correlates to the lowest dissociation limit Hg ($^{1}S$) and X($^{2}P_{3/2}$). The first electronically excited-state (A $^{4}\Pi$) of the halogenated radicals (Figure 2a and Figure S1), which is the most relevant for the present work, is strictly repulsive as noted in previous calculations of Wadt.\textsuperscript{12}

The repulsive character of this state, which has received little attention, can be interpreted based on two factors: (i) a charge-transfer component from the halogen atom to Hg (due to electron promotion from the atomic-like $p$ orbital of the halogen atom to the $\sigma^{6}$ONO (see Figure 1)), which neutralizes the charge separation of $X \Sigma^+$ ground state and decreases the Coulombic attraction and (ii) the orbital populated ($\sigma^{6}$ONO) has antibonding character. Light absorption (in the 600–700 nm range, see below) would photodissociate the radicals into Hg($^{1}S$) and X($^{2}P_{1/2,3/2}$) atomic fragments with 100% efficiency.

The first bound excited-state of the monohalide series, $B^{2}\Sigma^+$ in Figure 2, is an ion-pair\textsuperscript{12} fluorescent state which yields the well-known lasing emission.\textsuperscript{28–30} The strong Coulombic binding interaction is reflected in the high calculated $D_0$ values (Table S1 and Figure S3), which only show a modest decrease from 428 in the chlorine radical to 401 kJ mol$^{-1}$ in the iodine radical, in agreement with experimental observations.

The MS-CASPT2 computed absorption spectra of the mercury monohalides and hydroxyl radical species are presented in Figure 3 (see also Tables S4–S13), for the wavelength range of atmospheric relevance. In addition, numerical cross-section values, with 1 nm resolution, are

![Figure 1](image1.png)

Figure 1. Natural orbitals (isovalue = 0.05) of HgX (X = Cl, Br, I, and OH).

![Figure 2](image2.png)

Figure 2. Potential energy curves including SO-effects of the low-lying electronic states of HgBr (a) and HgOH (Hg–OH stretching) (b) as a function of the internuclear distance. SF labels are used here.
The light-colored areas correspond to the uncertainty of the cross-section due to the statistical sampling. Note the different range of \( \sigma \) values for the spectra.

The computed SO splitting of the \( ^2\Sigma^+ \) multiplet \( \rightarrow \Pi \) doublets may be explained by an excitation more localized on the \( \text{Hg} \) atom. The photolysis of \( \text{HgBr} \), globally integrated in the 240–520 nm range \( (\text{band A}) \) arises from SO coupling effects, which split each of the \( 2 \Pi \) SF transitions into SO pairs, with \( \Omega \) values of 1/2 and 3/2 (Figure 1; Tables S6, S8, and S10). These sharp C–D doubllets may be explained by an excitation more localized on the \( \text{Hg} \) atom.

For the dissociative band \( A^2\Pi \), the calculated SO splitting increases from 0.09 eV (\( \text{HgCl} \)) to 0.3 eV (\( \text{HgBr} \)), maintaining similar absorption intensity (Tables S6 and S8), which explains the larger bandwidth of this band in the latter. The splitting is even larger in \( \text{HgI} \) (0.59 eV, Table S10) and the transition connected with the \( \Omega = 1/2 \) state becomes much more favored resulting in an intensity increase of the photodissociative band \( A^2\Pi \) (Figure 3). See SI for further details.

The absorption cross-sections of \( \text{HgCl} \), \( \text{HgBr} \), \( \text{HgI} \), and \( \text{HgOH} \) in the 270–800 nm range, excluding the 270–460 nm interval corresponding to non-dissociative transitions to the states B, C, and D, were introduced into a global chemistry-climate model, CAM-Chem, to compute the photolysis rate \( (1/s) \) of each species. The global tropospheric rate of photolysis is \( 6 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), \( 3 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), \( 2 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), and \( 1 \times 10^{-17} \) cm\(^2\) s\(^{-1}\) for \( \text{HgI} \), \( \text{HgBr} \), \( \text{HgCl} \), and \( \text{HgOH} \), respectively. The competition between thermal-4 and photoreduction processes of \( \text{HgBr} \) and its oxidation reactions\(^{28} \) with the abundant radicals \( \text{NO}_2 \) and \( \text{HO}_2 \) (Scheme 1) was determined by calculating the averaged pseudo-first-order rates in the troposphere:

\[
\text{HgBr} + \text{NO}_2 \rightarrow \text{syn-BrHgONO} \quad (R1)
\]

\[
\text{HgBr} + \text{HO}_2 \rightarrow \text{BrHgOOH} \quad (R2)
\]

\[
\text{HgBr} \stackrel{\Delta\tau}{\rightarrow} \text{Hg} + \text{Br} \quad (R3)
\]

The photolysis of \( \text{HgBr} \), globally integrated in the troposphere, is of the same order \( (10^{-17} \text{ s}^{-1}) \) as the pseudo-first-order rates of oxidation by \( \text{NO}_2 \), R1 and \( \text{HO}_2 \), R2, and much faster than thermal decomposition R3. Therefore, the photolysis of \( \text{HgBr} \) will compete with oxidation by \( \text{NO}_2/\text{HO}_2 \) in places with high concentrations of these oxidants. The computed photolysis of \( \text{HgBr} \) would be faster than the reaction with \( \text{NO}_2/\text{HO}_2 \) in regions free of anthropogenic pollution,

\[
\times 10^{-17} \text{ cm}^2, \text{ respectively, consistent with those computed here for the gas-phase species.}
\]

In connection with the low-intensity absorption band in the 600–700 nm range (Figure 3), little or no experimental information could be found. A broad absorption continuum centered at \( \sim 600 \) nm detected in the \( \text{HgBr} \) transient absorption spectra\(^{34} \) was assigned to a dissociative transition (band A) predicted theoretically.\(^{32} \) Similarly, the very weak fluorescence at \( \sim 685 \) nm was assigned to the \( ^2 \Sigma^+ \rightarrow A^2\Pi \) transition in the same radical species,\(^{28} \) in agreement with the values computed here (Table S8).

From the analysis of the SF deconvolution of the computed SO MS-CASPT2 spectra \( (\text{Figures S4–S7}) \) and electronic structure \( (\text{Tables S5–S13}) \), bands C–D, B, and A of the monohalide series can be assigned to the \( \Sigma^+, \Sigma^-, \Sigma^+ \rightarrow \Pi \) transitions, respectively. These transitions correspond essentially to one-electron promotion from the orbital with the unpaired electron \( (\sigma_{\text{ONO}}^+) \), mainly localized on the 6s \( \text{Hg} \) atomic orbital \( (\text{Figure 1}) \), to the \( \sigma_{\text{ONO}}^+ \) \( \text{Hg} \) (band C–D), from the \( \pi_{\text{xy}} \) of the halogen atom to the \( \sigma_{\text{ONO}}^+ \) (band B), and from \( \sigma \) bonding orbital to the \( \sigma_{\text{ONO}}^+ \) (band A). The doublet at \( \sim 280 \) nm \( (\text{bands C and D}) \) and the large bandwidth of the absorption in the dissociative 600–700 nm range \( (\text{band A}) \) arise from SO coupling effects, which split each of the \( 2 \Pi \) SF transitions into SO pairs, with \( \Omega \) values of 1/2 and 3/2 \( (\text{Figure 1}; \text{Tables S6, S8, and S10}) \). These sharp C–D doubllets may be explained by an excitation more localized on the \( \text{Hg} \) atom.

The absorption cross-sections of \( \text{HgCl} \), \( \text{HgBr} \), \( \text{HgI} \), and \( \text{HgOH} \) in the 270–800 nm range, excluding the 270–460 nm interval corresponding to non-dissociative transitions to the states B, C, and D, were introduced into a global chemistry-climate model, CAM-Chem, to compute the photolysis rate \( (1/s) \) of each species. The global tropospheric rate of photolysis is \( 6 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), \( 3 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), \( 2 \times 10^{-17} \) cm\(^2\) s\(^{-1}\), and \( 1 \times 10^{-17} \) cm\(^2\) s\(^{-1}\) for \( \text{HgI} \), \( \text{HgBr} \), \( \text{HgCl} \), and \( \text{HgOH} \), respectively. The competition between thermal-4 and photoreduction processes of \( \text{HgBr} \) and its oxidation reactions\(^{28} \) with the abundant radicals \( \text{NO}_2 \) and \( \text{HO}_2 \) (Scheme 1) was determined by calculating the averaged pseudo-first-order rates in the troposphere:

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Scheme 1. The Residence Time of Elemental Mercury Hg(0) in the Atmosphere Is Determined by the Competition between the Rates of Reduction and Oxidation of the HgBr Radical.

\( \text{h}_0 \xrightarrow{\Delta t} \text{Hg(0)} \xrightarrow{\Delta t} \text{Br} \xrightarrow{\Delta t} \text{HgBr} \xrightarrow{\Delta t} \text{HgBr}_2 \)

“The new HgBr photoreduction process proposed in this study is highlighted in blue.

where NO₂ levels are low, such as the open ocean environments and the mid- to upper-troposphere.

The novel photochemistry of gas-phase Hg(I) radical species has broad implications for atmospheric mercury chemistry. This photoreduction process has been largely overlooked, and our findings suggest that the photolysis of Hg(I) will increase the atmospheric lifetime of mercury, which is key to understanding the global atmospheric mercury cycle. Current atmospheric mercury models, which do not include HgBr photolysis, are clearly underestimating the lifetime of mercury in the atmosphere. Overall, the new findings on the photochemistry of Hg(I) radicals reported in this Communication challenge current kinetic models of atmospheric mercury chemistry.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b02890.

Computation details, electronic structure tables, thermochemical data and deconvoluted spectra (PDF)
Cross-section data (XLSX)

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Notes
The authors declare no competing financial interest.

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