



# Mechanism of mercury-iodine species binding on carbonaceous surface: Insight from density functional theory study



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## HIGHLIGHTS

- Density functional theory is used to study the mercury-iodine binding mechanism.
- The interactions of HgI and HgI<sub>2</sub> with different sites on surface are considered.
- Adsorption energies, bond population and schematic energy profiles are calculated.
- The adsorption of HgI and HgI<sub>2</sub> on carbon surface is mainly chemisorption.

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## ABSTRACT

Iodated activated carbons were found to be effective for the mercury uptake from coal combustion flue gas. However, the detailed mechanism of mercury binding remains unclear. The adsorption mechanisms of mercury iodine on carbonaceous surface were studied by density functional calculations. A cluster model of five benzene rings was used to represent the active sites. The Mulliken bond population and total atomic charges analysis were performed to better understand the interaction of mercury-iodine species with surface. The results show that the binding of mercury-iodide species on surface include several adsorbing and desorbing processes. HgI is strongly adsorbed on the surface and the preferred adsorption mode is Hg-down mode. HgI is very stable existing on surface because the evolution of HgI is highly endothermic process. HgI<sub>2</sub> adsorption is not stable, and some of the geometrical configurations of the intermediates show the dissociation of HgI<sub>2</sub>. The dominant interaction pathway is the dissociation of HgI<sub>2</sub> with the binding of HgI and I on carbon surface.

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## 1. Introduction

Mercury is considered to be one of the most toxic metals found in the environment because of its bio-accumulative effect, high volatility, neurological health impacts and global range transportation [1]. The large quantity and scale of coal-fired boilers make coal burning the largest source of mercury emissions related to human activity [2]. Thus the development of efficient methods for the control of mercury emissions from coal-fired power plants is an urgent and global concern.

Choosing appropriate sorbents is an essential key to reduce mercury emission from coal-fired power plants [3]. It has been found previously that the impregnation of activated carbon using halogen is able to improve their mercury uptake efficiency, especially for the power plants with a low chlorine concentration in

flue gas [4,5]. In particular, iodine has a lower vapor pressure at ambient temperatures. This makes iodine safer to store and transport as it is a solid. Iodated activated carbons were found to be an effective sorbent for Hg<sup>0</sup> capture. De et al. [6] impregnated activated carbon by applying various halogen ions, including KCl, KBr, KI and NH<sub>4</sub>I, and found that I-impregnated carbon had the largest removal efficiency. Chi et al. [7] investigated the influence of iodine on Hg<sup>0</sup> removal, and found that the iodine impregnated activated carbon showed the most effective Hg<sup>0</sup> capture, about 7% higher than that for activated carbon impregnated with bromine. X-ray absorption fine structure (XAFS) results made by Huggins et al. [8] showed that iodine is an activating element and forms a sorption complex with mercury. Furthermore, they found mercury can be captured by bonding to I anionic species on the carbon surfaces by X-ray absorption near-edge structure (XANES) spectra [9]. Lee et al. [4] have investigated the Hg<sup>0</sup> uptake ability of iodine- and chlorine-impregnated activated carbons by applying a laboratory-scale fixed-bed reactor. They found that the I-impregnated

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activated carbons were effective for  $\text{Hg}^0$  removal, but the  $\text{Hg}^0$  capture efficiency was not proportional to the concentration of iodine. Both XPS analysis and SEM-EDS results confirmed the presence of the mercury compound. It is supposed that the reaction of Hg with I-impregnated carbon can be considered as the producing of HgI firstly and then the reaction of HgI with carbon surface. For the purpose of enhancing interaction of mercury with carbon, the injection of iodated carbon is commonly conducted in the air pre-heater. During the flue gas cooling, the mercury will be oxidized to HgI and  $\text{HgI}_2$  first and then be adsorbed on carbon.

Although the adsorption of mercury on iodated carbon has been studied experimentally, theoretical study on the mechanism of mercury adsorption on iodated carbon has still been limited [10]. Nowadays, quantum chemical calculations have become one of the most accurate theoretical methods for studying the structure, energy and geometrical parameters for reactants and products [11–14]. It can provide reaction energies and propose possible surface intermediates. The oxidation and adsorption processes of mercury on different solid surfaces, including vanadia-titania catalyst [15,16], and Au, PdAu, PdAg, PdCu metal surfaces [17,18], have been investigated by performing theoretical calculations. Padak and Wilcox [19] studied the adsorption mechanisms of Hg-Cl species on activated carbon by applying density functional theory calculations and a cluster model of the carbon surface. In our previous studies [20], the effect of bromine on mercury adsorption on carbonaceous surface was studied by density functional theory. The effect of  $\text{SO}_2$  on mercury adsorption on carbonaceous surface was investigated [21]. However, to date, there is no theoretical study involving mercury-iodine species adsorption on carbonaceous surface at the molecular level.

The mercury-iodine species is important for the mercury uptake by iodated activated carbon. Understanding the detailed adsorption mechanism of Hg on sorbent is important to the design of more effective carbon sorbents for mercury removal in coal combustion flue gas [22,23]. In this paper, density functional theory was employed to examine the effects of adsorbed I on  $\text{Hg}^0$  adsorption and the adsorption properties of HgI and  $\text{HgI}_2$  on carbonaceous surface, aiming to explore the mechanism of mercury transformation and mercury-iodine species binding on carbonaceous surface.

## 2. Computational details

### 2.1. Methodology

In our previous work [24], different combinations of quantum mechanical method with basis set have been validated. The results indicated that B3PW91/RCEP28DVZ combination provided reasonably accurate results for the systems involving mercury. Therefore, B3PW91/RCEP28DVZ was employed for the Hg and I atom in this study. The 6-31G (d) basis set was used to describe C and H atoms.

Gaussian03 software package was used to perform theoretical calculations [25]. The adsorption energy ( $E_{\text{ads}}$ ) of an adsorbate “A” on a solid surface “B” can be calculated as:

$$E_{\text{ads}} = E(\text{AB}) - (E(\text{A}) + E(\text{B})) \quad (1)$$

where  $E(\text{A})$  is the total energy of the adsorbate,  $E(\text{B})$  is the total energy of the substrate, and  $E(\text{AB})$  is the total energy of adsorbate/substrate system in equilibrium state. A negative value of  $E_{\text{ads}}$  indicates that the adsorption is an exothermic process. Normally, if the adsorption energy is less than  $-30$  kJ/mol, the interaction belongs to physisorption. If the adsorption energy is higher than  $-50$  kJ/mol, the interaction belongs to chemisorption [26].

### 2.2. The cluster model

The finite clusters are used to represent carbonaceous surface. Carbonaceous materials are commonly consisted by 3–7 benzene rings from solid-state  $^{13}\text{C}$  NMR experiments [27]. By using different size of clusters, the accuracy analysis of molecular systems showed that the reactivity of the carbonaceous model does not rely deeply on the molecular size [28]. The reactivity relies more deeply on the local shape of the active site rather than the size of the model [29]. In addition, the edge sites are more active than the center sites [10]. Therefore, the carbonaceous surface was represented by a five fused benzene rings. The optimized bond lengths of C–C and C–H are 1.41 Å and 1.09 Å respectively, which are consistent with the experimental results (1.42 Å and 1.07 Å) [30], indicating that the model are reliable.

## 3. Results and discussion

### 3.1. The adsorption of $\text{Hg}^0$ on I-carbonaceous surface (CS)

Fig. 1 shows the model of  $\text{Hg}^0$  interacting with I-CS.  $\text{Hg}^0$  adsorption on CS is mainly physisorption with an adsorption energy of  $-44.6$  kJ/mol. The binding energy of  $\text{Hg}^0$  on I-CS is found to be  $-66.9$  kJ/mol, indicating that the adsorption of  $\text{Hg}^0$  on I-CS belongs to chemisorption. Lee et al. [31] performed the  $\text{Hg}^0$  removal experiments by I-treated carbons, and found that  $\text{Hg}^0$  removal efficiency of I-treated carbons increased with increasing of temperature and this phenomenon was commonly associated with a chemisorption mechanism. Li et al. [32] carried out experiment to investigate the removal of Hg by halides modified bio-chars, and suggested that C–I was chemisorption site for Hg adsorption. The calculation result of chemisorption agrees well with the experimental data. Therefore, The embedding I atom on CS promoted the adsorption of  $\text{Hg}^0$ .

Moreover,  $\text{Hg}^0$  prefers to interact with the carbon atom neighboring to I atom because the adsorbed I atom can draw electrons from the surface carbon atoms. This makes the atomic charges of these carbon atoms more positive. The improvement of  $\text{Hg}^0$  capture on iodated activated carbon is owing to the charge transfer. The XPS and XAS experiments suggest that mercury is bound with the iodide sites on the carbon surface [33], which agrees well with our results.

### 3.2. The adsorption of HgI on carbonaceous surface

In order to examine the adsorption mechanism of HgI on CS, HgI interacts with different sites in various situations were shown in Fig. 2. All the possible orientation were considered including HgI approaching the carbon surface in Hg-down mode, I-down mode and side-on mode. The possible structures are illustrated in Fig. 2.

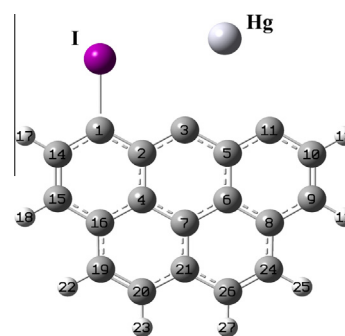


Fig. 1. The optimized structure of  $\text{Hg}^0$  adsorption on I-CS.

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