Research paper

Adsorption of the astatine species on a gold surface: A relativistic density functional theory study

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ABSTRACT

We report first-principle based studies of the adsorption interaction of astatine species on a gold surface. These studies are aimed primarily at the support and interpretation of gas chromatographic experiments with superheavy elements, tennessine (Ts, $Z = 117$), a heavier homologue of At, and possibly its pseudo-homologue nihonium (Nh, $Z = 113$). We use gold clusters with up to 69 atoms to simulate the adsorption sites and estimate the desorption energies of At & AtOH from a stable gold (1 1 1) surface. To describe the electronic structure of $At - Au_n$ and $AtOH - Au_n$ complexes, we combine accurate shape-consistent relativistic pseudopotentials and non-collinear two-component relativistic density functional theory. The predicted desorption energies of At and AtOH on gold are 130 ± 10 kJ/mol and 90 ± 10 kJ/mol, respectively. These results confirm the validity of the estimates derived from chromatographic data (147 ± 15 kJ/mol for At, and 100^{+20}_{-10} kJ/mol for AtOH).

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1. Introduction

The discovery of relatively long-lived isotopes of superheavy elements (SHEs) in ^{48}Ca-induced nuclear fusion reactions [1] shows that the shore of the island of particularly shell-stabilized nuclei has indeed been reached [2,3]. While the recent addition of four new elements to the periodic table [4] is a fantastic discovery in itself, the long half-lives of certain isotopes open up the possibility for chemical investigations. Hence, after successful chemical characterization of elemental copernicium (Cn, $Z = 112$) [5] and flerovium (Fl, $Z = 114$) [6], nihonium (Nh, $Z = 113$) increasingly catches chemists' interest. First experimental results have been recently obtained at the Flerov Laboratory of Nuclear Reaction in Dubna, Russia [7,8].

On-line gas-phase thermochromatography is a unique method for chemically studying the usually very short-lived SHEs at a one-atom-at-a-time regime [9,5]. These experiments are extremely sophisticated and, moreover, they are confronted by rather low statistics for determining the corresponding chemical properties of the SHE in question. Thus, reliable preliminary theoretical modeling is essential for the experimental success as well as for the correct and detailed interpretation of the available data.

From a theoretical standpoint, investigations on the properties of SHEs are especially challenging as they require a profound understanding of the electronic structure in the presence of strong fields of the heavy nuclei [10]. Relativistic effects may lead to dramatic dissimilarities in the chemical behavior of SHEs when comparing them to their lighter homologues. The calculated desorption energy for single atoms of nihonium on gold surface [11] ($E^{Au}_{des}(Nh) = 105 \pm 10$ kJ/mol) differs substantially from the experimentally measured desorption energy on gold of its nearest homologue thallium, $E^{Au}_{des}(Tl) = 262 \pm 6$ kJ/mol [12]. This raises the question of what one may learn from experiments with the lighter homologues of nihonium in terms of understanding the SHE's chemistry. Hence, finding a chemical pseudo-homologue with similar adsorption behavior appears a promising alternative.

It has been shown experimentally that the desorption temperatures and energies of Cn [5] and Fl [6] atoms on a gold surface are fairly close to each other and overall lower than those of their immediate homologues Hg and Pb observed on the same surface. This confirms theoretical predictions concerning the electronic structure of Cn and Fl atoms: the strong relativistic stabilization of the s- and $p_{1/2}$-shells in both Cn ($6d^{10}7s^2$) and Fl ($6d^{10}7s^27p^2_{1/2}$) results in a closed-shell character of the ground states of these atoms [13]. Due to this unique feature of the 7th row of

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the periodic table, the electronic structure of a Nh atom can be interpreted as a Fl atom with a hole in a closed $7p_{1/2}$-subshell [14]. This observation makes astatine a closer chemical "relative" of Nh than the formal homologue Tl. Thus, At is a plausible chemical species for model experiments aiming at finding the optimum experimental conditions for further explorations of the Nh chemistry.

The non-observation of any decays of Nh in the latest chemical experiment [8] requires a modification of the experimental approach. Therefore, future experimental efforts may focus primarily on the efficient formation and detection of NhOH molecules – most likely the chemical species observed in the early investigations [7]. A study of the electronic structure of NhOH and AtOH molecules has been carried out earlier at the combined one-component coupled cluster CCSD(T) and two-component relativistic functional theory (2c-RDFT) level [14]. The calculated enthalpies of the hydroxyl-group elimination at 0 K for both of these molecules are fairly similar (188 kJ/mol for NhOH and 174 kJ/mol for AtOH) and much smaller than the corresponding value for Tl (319 kJ/mol).

In this work, we make an attempt to estimate the desorption energies of single atoms of At and of AtOH molecules from a gold (1 1 1) surface. The results are directly compared to the desorption energies of astatine species (presumably elemental astatine and astatine hydroxide AtO_xH_y) from a gold surface, derived from gas chromatography data using Monte-Carlo simulation [15].

2. Method and computation details

To simulate the electronic structure of the $At/AtOH – Au_n$ adsorption complexes, we combine accurate shape-consistent relativistic pseudopotentials (RPPs) [16] and non-collinear 2c-RDFT [17] with two qualitatively different approximations for the exchange–correlational functional, namely, the generalized-gradient B88P86 [18,19] and the partially non-empirical hybrid PBE0 [20]. The RPP model allows to replace a rather complicated problem of the relativistic interacting electron gas in the strong nuclear field by a much simpler problem defined by the RPPs treating the state of the electron gas in the external field as formally non-relativistic, all at the cost of a rather complex external field structure. This replacement is accompanied by a sharp reduction of the number of variables (the wave functions depend only on the coordinates of the valence electrons) and by the elimination of the difficulty to approximate oscillations of the wave function in the vicinity of the atomic nuclei. RPPs are used for the representation of 60 core electrons of both, Au [21] as well as At [14]. The valence electrons, 19 for Au and 25 for At, are explicitly described within the (7s6p6d1f)/[5s5p4d1f] Gaussian basis set for Au and the (7s12p6d1f)/[5s8p4d1f] for At. Triple-zeta contracted Gaussian basis sets are used for H and O [22]. The resulting basis was shown

to be flexible enough for neglecting the basis set superposition errors.

Several gold clusters comprising up to 69 atoms were chosen to simulate the adsorption site of At/AtOH on the most stable gold (1 1 1) surface. These clusters were selected as near-surface fragments of an ideal gold crystal, with the Au–Au distances kept at their experimental crystal values. The errors arising from the neglect of relaxation of Au macrocrystal surface near the adsorption site for moderate binding energies should not exceed a few kilojoules per mole [23] and can be neglected at the present level of electronic structure modeling accuracy. One should notice, however, that such errors can be significant for At interaction energies with relatively small clusters, so the values for non-deformed finite clusters reported here should not be considered as reliable estimates for binding energy of an At atom with real gold nanoclusters (cf. Ref. [24]).

Fig. 1 illustrates the possible positions of the At atom on the surface of different gold clusters at the extremum points on the $At – Au_n$ potential energy surface. The respective equilibrium distance between the adsorbed At atom and the gold clusters is calculated separately for each of the adsorption complexes. In the case of the adsorption of AtOH on a gold cluster the equilibrium positions of the molecule are determined by allowing the molecule to move over the cluster surface. Based on a series of preliminary calculations, two competing positions of the AtOH molecule on the Au cluster surface are found (see Fig. 2). In the first case, the formation of a chemical bond between At and gold atoms occurs, whereas in a second case the bonding is mainly associated with a charge redistribution on the cluster surface. Since the stabilization of binding energies upon increasing the cluster size n can be occasional, the convergence is additionally monitored by analyzing the Bader net charge [25,26] of the astatine atom as well as the equilibrium distance At–gold as functions of the cluster size. The applicability and overall accuracy of the used basis sets and the calculation technique has been demonstrated in Refs. [14,23].

3. Results and discussion

3.1. $At – Au_n$ interactions

The calculated bond length R_e of AtAu molecule in the B88P86 approximation for the exchange-correlational functional is $R_e = 2.644$ Å and $R_e = 2.621$ Å for PBE0. The dissociation energy of the AtAu molecule is 190 kJ/mol for the B88P86 case and 180 kJ/mol for the PBE0 case. The chemical bond is formed without significant charge transfer.

For the more complex case of the adsorption of At on the surface of an Au cluster, Fig. 3 illustrates the dependence of the calculated At–Au_n binding energies and the Bader net charges of At in the different generic positions as functions of the inverse cluster size. It
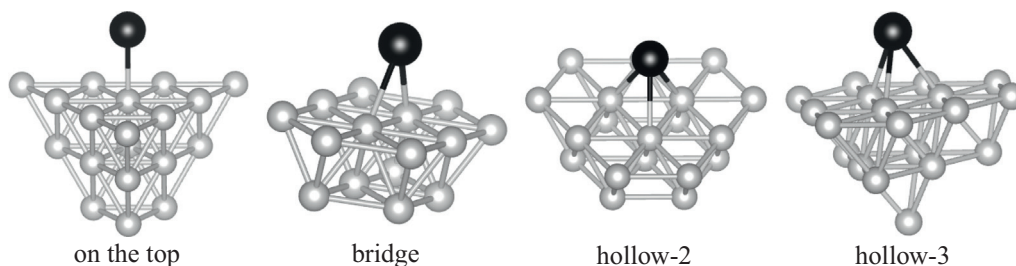

on the top   bridge   hollow-2   hollow-3

Fig. 1. The various types of considered $At – Au_n$ complexes, corresponding to the different possible positions of the At atom (black sphere) bonded to one, two, or three gold atoms (gray spheres): "on the top", "bridge", and "hollow". In the latter case, one has to discern the positions of the At atom with respect to the gold atom directly underneath in the second ("hollow-2") or third ("hollow-3") layer from surface.