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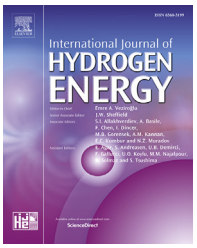

On the covalence in H_2–AuX (X = F–I)

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ABSTRACT

Theoretical investigations on the H_2–AuX (X = F–I) series have been performed at the CCSD(T) theoretical level with extended basis sets and the T-shaped stable structures were found. Mechanisms of Au-X and Au···H_2 interactions were explored by NBO analysis, natural resonance theory, electron density deformation analyses, delocalization index and visualized by reduced density gradient analyses. Periodic trends are found in the bond length, stability and covalent nature of the Au-X interactions. For Au···H_2 interactions, the delocalization index values and the electron density difference analysis show the "charge-shift covalent" type of interaction.

Introductions

What has attracted our interest is the noble gas-coinage metal halides, Ng-CmX (Ng = Ar, Kr, Xe; Cm = Cu, Ag, Au; X = F, Cl, Br, I) and polyatomic molecules-coinage metal halides, Pam-CmX (Pam = OH, H_2O, H_3N, H_3P) investigated by experiment and theory [1–15]. Through spectroscopic measurements and quantum chemical calculation, the Ng-Cm interaction in these complexes was found to be weakly covalent. We extended the investigation to the interaction between the heaviest experimentally known noble gas Rn and AuX; it suggests the intermediate type of moderate strength interaction with somewhat covalence [16]. Recently Obenchain and co-workers reported experimental and theoretical investigations on H_2–AuCl complex. The value of nuclear quadrupole coupling constant claims a strong, covalent interaction between Au and dihydrogen, Au···H_2. The dissociation energy (D_e), 147 (3) kJ/mol in experiment and 164 kJ/mol calculated at the MP2 theoretical level, falls into the range of a weak covalent Au···H_2 interaction [17]. In the H_2–AuCl complex, the free H_2 molecule interacts with the Au atom (or AuCl), namely, the Au atom interacts with the H–H bond; it is different from those in Ng–CmX series that the Cm atoms interact with the Ng atom(s) directly. It would be meaningful and interesting to give a description of structures and properties of this class of compounds. Our previous studies [18] clearly demonstrate that the natural bond orbital (NBO) [19,20], Atoms in Molecules (AIM) theory [21] and topological analyses on electron density properties, such as the electron density deformation and Laplacian are powerful utilities to explore mechanisms of interaction between atom pairs. Shahbazian and co-workers [22,23] suggested to rename (3, -1) critical points as "line" critical points (LCP) and the corresponding path as "line" paths, the nature can be described to some extent by descriptors such as the electron density, Laplacian $\nabla^2\rho$ and energy density $E(r)$ at LCP.

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Electrostatic potential (ESP) on the 0.001 e/bohr^3 molecular surface is helpful for predicting structures [24]. CCSD(T) calculations on AuCl and H_2 molecule show the existence of positive ESP maxima in the extremes along the Cl–Au axes (81.86 kcal/mol) and negative ESP maxima (−3.50 kcal/mol) in the equatorial zone of H_2 molecular surface, respectively. The free H_2 molecule is expected to form T-shaped stable H_2–AuX (X = F–I) complexes with the top of the T being the H_2 ligand as displayed in Fig. 1. It presents a convenient model to investigate the nature of Au···H_2 and Au-X interactions. In this study, systematic CCSD(T) and MP2 theoretical studies on H_2–AuX (X = F–I) series were performed to predict the structures and stabilities, and obtain further insights into the covalence of Au···H_2 and Au-X interactions. Meanwhile, hydrogen has attracted considerable interest in both experiments and theories as a clean, abundant energy carrier [25–29]. The major interest for its application in transportation is the development of an inexpensive and safe storage way [30,31]. It is expected to be helpful in hydrogen storage and application.

Computational details

Theoretical description of systems that involve weak interaction is sensitive to basis set quality and to the level at which electron correlation is accounted for. It is confirmed that electron correlation at the CCSD(T) level with large basis sets (the inclusion of high angular momentum functions) is required to achieve high accuracy [32,33]. The 19-valence electron basis sets *(37s33p22d2f1g)/[5s5p4d2f1g]* and matching relativistic pseudo-potentials were employed for Au atom [34]. For H, F and Cl atoms, all electron basis sets aug-cc-pVQZ were employed [35,36]. The 25-valence electron basis sets *(33s26p14d3f2g)/[7s6p5d3f2g]* and corresponding relativistic pseudo-potentials were employed for Br and I atoms [37].

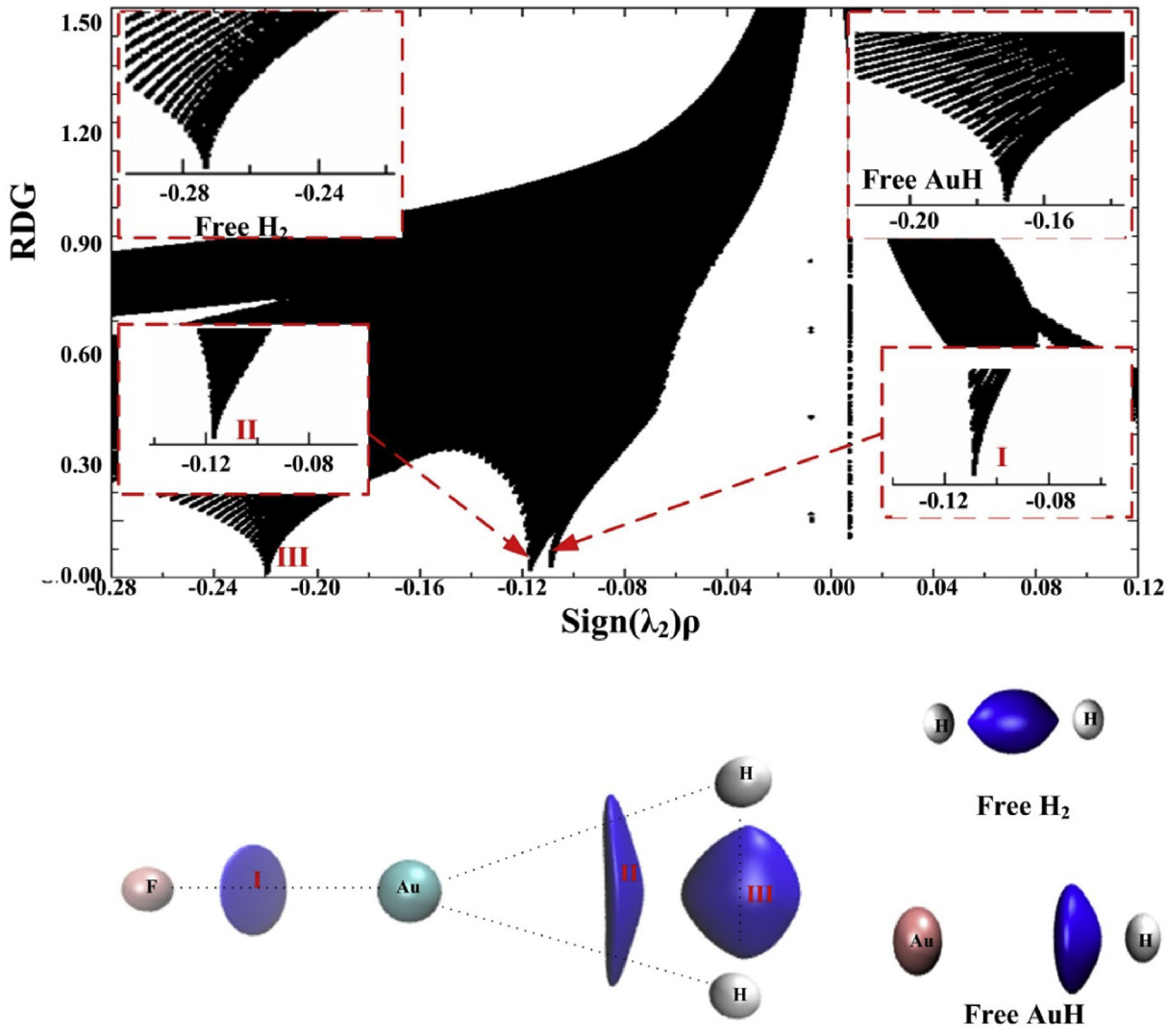

Fig. 1 – Plots of the reduced density gradient (RDG) *vs* sign $(\lambda_2)\rho$ (Upper panel) and RDG isosurfaces (Lower panel) for H_2–AuF together with those of the free H_2 and AuH for comparison. The surfaces are colored on a blue-green-red scale according to values of sign $(\lambda_2)\rho$. Blue isosurface indicates attractive interaction. (For interpretation of the references to color/colour in this figure legend, the reader is referred to the Web version of this article.)

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