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Regular Article

Benchmarking Density Functional Theory for Noble Metal Hydrides: A High-Fidelity PES and Vibrational Analysis of the $AgAuH^-$ Anion

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Abstract: The accurate description of noble metal hydrides remains a fundamental challenge for electronic structure theory, especially in systems involving heavy elements where relativistic effects and electron correlation are significant. In this study, we present a high-accuracy potential energy surface (PES) for the $AgAuH^-$ anion, constructed from 3,595 UCCSD(T)-F12a energy points and fitted using a feedforward neural network with a root mean square error of 0.21 meV. The PES captures the entire configuration space, including linear and bent minima, transition-state-like structures, and dissociation pathways. Quantum vibrational bound states were computed using time-independent quantum dynamics, enabling detailed mode assignments. The high-fidelity PES and vibrational dataset were used to benchmark some widely employed density functional theory (DFT) methods, B3LYP, ωB97XD, XYG3, and XYGJ-OS. Among these, XYGJ-OS provided the best agreement with the reference data in terms of equilibrium geometries and vibrational frequencies. This study provides a robust benchmark for method development and validation in metal-containing systems and highlights the importance of using high-level reference data when modeling complex coinage-metal hydrides.

Key words: $AgAuH^-$, density functional theory benchmarking, high-level *ab initio* potential energy surface, vibrational quantum dynamics, coinage metal hydrides.

1. Introduction

Gold and silver cluster compounds are key systems in catalysis, hydrogen storage, and photochemistry [1-4]. Due to their complex electronic structures and significant relativistic effects, accurate theoretical characterization remains challenging [5]. While density functional theory (DFT) is widely used due to its computational efficiency, most studies rely on low-rung functionals and static structures, leaving uncertainties regarding the predictive power of different methods [6]. In particular, the performance of DFT for systems containing coinage metals is highly functional-dependent, and systematic benchmark studies against high-level *ab initio* data are rarely reported [7-9].

Theoretically, the $AgAuH^-$ anion presents an ideal prototype to probe fundamental bonding, relativistic effects, and the reliability of electronic structure methods [10]. Its simplicity as a three-atom system allows for high-level quantum chemical treatment while still encapsulating the essential features of noble metal bonding. In addition, experimental photoelectron spectra of AgAuH are feasible, but accurate vibrational assignments and spectroscopic interpretation remain incomplete, primarily due to the absence of reliable theoretical reference data.

A critical limitation in the field is the lack of benchmark datasets that combine high-fidelity potential energy surfaces (PESs) with corresponding vibrational state data. Such datasets are essential for testing and calibrating DFT and other computational methods. Given the increasing role of machine-learned PESs in molecular dynamics, having robust *ab initio*-based datasets is also indispensable for training and validating surrogate models [11,12].

In this study, we construct a high-accuracy PES for the $AgAuH^-$ anion based on CCSD(T)-F12a/aug-cc-pVTZ level of theory [13] and fitted using a feedforward neural network [14,15]. The resulting surface allows for precise vibrational state calculations using time-independent quantum dynamics. The computed dataset serves as a benchmark to systematically evaluate the performance of widely used DFT functionals, including B3LYP [16-18], ωB97XD [19], XYG3 [20], and XYGJ-OS [21], regarding structural, energetic, and vibrational predictions, providing a valuable reference for future spectroscopic and dynamical investigations.

The organization of this paper is delineated as follows: Section 2 provides an overview of theoretical methods, including PES construction and vibrational bound state calculations. In Section 3, a comparative analysis of the PES and vibrational states is conducted alongside the comparisons between density functional approximations and the CCSD(T) method, and discussions are made on the accuracy and availability of density functional approximations in the construction of high-level PESs. Finally, we conclude the paper in Section 4.

2. Theoretical method

2.1 Electronic structure calculations

All reference energy points were computed using the CCSD(T)-F12a method [13] with the aug-cc-pVTZ (augmented correlation-consistent polarized valence triple-zeta) basis set [22] for H and the aug-cc-pVTZ-PP (with pseudopotential) basis set [23] for Ag and Au. All coupled cluster calculations were performed using the MOLPRO 2020.1 software [24]. The dataset consists of 3,595 symmetry-unique geometries distributed over a broad configuration space, including both near-equilibrium and highly distorted geometries. These points were selected to uniformly sample the relevant bond lengths and angles to ensure global PES coverage.

In addition to the CCSD(T)-F12a calculations, two commonly used DFT methods, B3LYP [16-18], ωB97XD [19], as well as a series of xDH-type doubly hybrid functionals such as XYG3 [20] and XYGJ-OS [21], were also employed for comparison. Optimized geometries, harmonic frequencies, and single-point energies were obtained using these functionals with the same basis sets and pseudopotentials, ensuring consistency with the reference calculations. All DFT calculations were completed using a modified version of the Gaussian 16 program [25].

2.2 Neural network potential energy surface

A feedforward neural network (NN) model with architecture 3-30-30-1 was used to fit the PES [14,15,26]. Since the AgAuH system consists of three distinct atomic elements, permutation invariance among identical atoms is not a consideration. Therefore, the three internuclear distances (Ag-Au, Ag-H, and Au-H) were used directly as input features for the NN function. The network was trained using 90% from the CCSD(T)-F12a data set, with the remaining 10% reserved for validation. The final NN PES achieved a root mean square error (RMSE) of 0.21 meV, indicating excellent agreement with the high-level reference data throughout the full-dimensional configuration space. Details of the NN PES constructions can be found in our previously reported works [14,15,26-29].

2.3 Vibrational state calculations

Vibrational bound states were computed using a time-independent quantum dynamics approach. The nuclear Schrodinger equation was solved using discrete variable representation (DVR) in Jacobi coordinates (as illustrated in Figure 3). Specifically, a dense sampling of 199 points was used for the $R_{\text{Ag-Au}}$ distance, covering the range from 4.2 to 7.5 bohr, and likewise, 199 points were allocated for the $R_{\text{H-COM}}$ coordinate, extending from 0.0 to 9.5 bohr. The Jacobi angle θ was described using 30 distinct points. Nearly 50 bound states were determined using the Lanczos algorithm [30], spanning both the $[\text{H-Ag-Au}]^-$ and $[\text{Ag-Au-H}]^-$ isomers. Quantum numbers (v1, v2, v3) were assigned based on mode character and nodal patterns.

2.4 DFT benchmarking

DFT performance was evaluated by comparing optimized geometries, vibrational frequencies, and selected vibrational energy levels to the benchmark CCSD(T)-F12a results. Special attention was given to the Ag-Au stretching mode and the H-bending mode, which were found to be most sensitive to the choice of the functionals. Deviation metrics including mean absolute error (MAE) and root-mean-square deviation (RMSD) were computed to quantify the agreement.

3. Results and discussion

3.1 The CCSD(T)-F12a reference dataset

3.1.1 Stationary geometries and potential energy surface

Figure 1 summarizes the key stationary points located on the CCSD(T)-F12a/aug-cc-pVTZ potential energy surface of the $AgAuH^-$ anion. The figure includes both linear and bent structures, representing local minima and transition-state-like configurations. Bond lengths are given in Å, bond angles in degrees, and relative energies in red (in eV), with respect to the global minimum. These structures provide insight into the topography of the PES relevant to vibrational and isomerization dynamics.

The linear $[\text{H-Ag-Au}]^-$ geometry is confirmed as the global minimum, while a higher-energy local minimum corresponding to the $[\text{Ag-Au-H}]^-$ isomer is also identified. Two bent structures serve as transition states connecting these minima and exhibit distinct bonding characteristics.

In transition State 1, the H-Ag bond is short (1.596 Å), whereas the Ag-Au bond is longer (2.772 Å), indicating that the hydrogen atom is more strongly bonded to Ag, while Au is partially dissociated. Conversely, in transition State 2, the Au-H bond becomes dominant (1.563 Å) and the Ag-Au bond shortens to 2.660