Ab Initio Study of Hg–Hg and E112–E112 Van Der Waals Interactions

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Received November 16, 2007; in final form, September 9, 2008

Abstract—The ground electronic state of the eka-mercury dimer (E112$_2$) was studied within the model of generalized relativistic effective core potentials. A combined procedure based on describing correlation effects by the scalar relativistic coupled-cluster method and on taking into account spin-dependent interactions by means of density-functional theory was used in the calculations. A high accuracy of this approach was confirmed by the results of similar calculations for the mercury dimer. It was found that the bond length is nearly 0.4 Å shorter in E112$_2$ than in Hg$_2$ and that the dissociation energy of the former is approximately twice as high as that of the latter dimer.

DOI: 10.1134/S1063778809030028

INTRODUCTION

In the past decade, considerable advances have been made in the synthesis of superheavy elements from the stability island (region of nuclei whose charge number $Z$ lies between 104 and 116) [1, 2], which possess unique chemical properties [3–5], primarily because of anomalously strong relativistic effects. An experimental study of the chemistry of superheavy elements is very complicated and laborious. Experimental results here are frequently ambiguous and sometimes contradictory. In view of this, theoretical predictions based on calculating the electronic structure of compounds of superheavy elements are required for choosing optimum conditions for separating and identifying such elements. The element 112 (eka-mercury) has attracted attention of researchers since the 1970s [6, 7]—in particular, in connection with the hypothesis of its extreme chemical inertness [6], which distinguishes this element sharply from ordinary mercury. Experiments aimed at a chemical identification of the isotopes E112 from the stability island had led to contradictory results before 2006, when it became possible to reduce the time of the on-line stage of the experiment to a few seconds [2]. Attempts at simulating the electronic structure of E112 compounds did not provide a reliable and unambiguous solution to the problem of its chemical activity. In particular, the investigation of the E112H molecule in the scalar relativistic approximation predicted [8] that E112 resembles an inert gas, while relativistic density-functional theory gives, for the energy of E112 binding with gold clusters Au$_n$, a value commensurate with that for a mercury atom [9].

Note that the calculations in question were performed by using a number of approximations not quite well justified for superheavy elements. A thorough analysis of all of those approximations and the elimination of insufficiently reliable ones in [10–12] led to results incompatible with the hypothesis of eka-mercury inertness.

Published forecasts concerning the properties of the E112 dimer and providing information that can be used to get an idea of the van der Waals radius of the E112 atom [13, 14] are markedly different. In this article, we present the results of a comparative ab initio investigation of the ground states of the E112$_2$ and Hg$_2$ systems, constructing an accurate description of correlation and relativistic effects.

COMPUTATIONAL PROCEDURE

The calculations were performed within the model of a generalized relativistic effective core potential (pseudopotential) [15]. Chemically inactive inner electron shells of the core (1s–4f for Hg and 1s–5f for E112) were excluded from the explicit consideration, and their interaction with the subsystem of valence electrons and outer core electrons was described in terms of a spin-dependent one-body operator. The wave function for this subsystem was constructed from two-component single-particle (pseudo)spinors. The pseudopotential version used

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in the present study effectively includes the spin–orbit and Breit interactions, as well as the Fermi distribution of the charge density in the nucleus [16].

A high precision in describing electron correlations is required for deducing reliable theoretical estimates of the properties of loosely bound van der Waals systems such as the Hg$_2$ and E112$_2$ molecules. We made use of a computational scheme that combines the derivation of a correlated solution to a many-electron problem by the coupled-cluster method in the scalar relativistic approximation [CCSD(T)] and with allowance for the spin–orbit correction [CCSD(T) + ∆E$_{SO}$], curve 2]. Curves 3 and 4 were calculated by the relativistic density-functional method with the aid of, respectively, the PW91 and PBE exchange–correlation functionals. The correlations of electrons in two σ orbitals consisting of the outer core atomic 5s orbitals of Hg (6s orbitals of E112) were disregarded (see the analysis of the contributions of correlations for various shells of Hg in [17]). The calculations were performed by using several basis sets of different dimension: (i) (14s 12p 9d 3f 2g)/[7s 7p 4d 3f 1g], (ii) (14s 12p 9d 3f 2g)/[10s 8p 5d 3f 2g], and (iii) (14s 12p 9d 5f 3g 2h)/[10s 9p 7d 5f 3g 2h] for the Hg$_2$ molecule and (i) (16s 21p 16d 12f 14g)/[4s 6p 4d 3f 2g] and (ii) (16s 21p 16d 12f 14g 2h)/[11s 10p 8d 5f 4g 1h] for the E112$_2$ molecule. We note that the direct inclusion of spin–orbit interaction within the coupled-cluster method with basis sets of such dimensions is overly cumbersome and that a substantial reduction of the basis dimension leads to large errors [13].

In calculating the energy properties of weakly bound van der Waals systems by methods that involve representing the operator of one-electron interaction in a finite basis, the basis-set-superposition error (BSSE) may be commensurate with the binding energy. In the present study, this error was eliminated approximately by means of counterpoise corrections [18]. We note that the smallness of these corrections serves as a criterion of the completeness of a basis set. In order to determine the contribution of spin–orbit interactions to the energy features of the dimers, we constructed potential–energy functions for Hg$_2$ and 112$_2$ by the relativistic density-functionals...