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Structural changes induced by an excess electron in small mercury clusters

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Abstract

We discuss structural differences between neutral and negatively charged mercury clusters, with cluster sizes ranging from Hg_3 to Hg_7. We have optimized various types of structures for both species using quantum chemical *ab initio* methods. Because of the binding character of the *p*-type orbital occupied by the excess electron we observed a contraction of the bond length of approximately 0.2 Å on average. This corresponds to changes of the binding energy of the excess electron of 0.1 to 0.4 eV. In addition to this we encountered changes in the relative stability for different structures of the same cluster size by attaching an excess electron. The consequences for a meaningful comparison between theory and experiment are discussed in terms of recent measurements of electron affinities for mercury clusters. Finally, we propose a hybrid model for the incorporation of electron correlation effects. It consists of pairwise additive effective dispersion potentials and configuration interaction calculations that take into account correlation contributions originating from the excess electron. Numerical tests have been performed for selected clusters and revealed good agreement with more accurate *ab initio* methods. (Int J Mass Spectrom 201 (2000) 197–204) © 2000 Elsevier Science B.V.

Keywords: Mercury clusters; Hybrid model; Electron affinity

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1. Introduction

The computational tools that are presently available in *ab initio* quantum chemistry make it possible to perform calculations for clusters that enable a quantitative comparison with experiment. Although the range of computationally accessible cluster sizes may vary considerably depending on the elemental constituents, the property of interest, and the desired accuracy, such calculations are now feasible—at least for small clusters.

From the very beginning, quantum chemical *ab initio* methods have been designed to achieve accuracies comparable to the most accurate experimental techniques. In order to calculate a given property measured in experiment, it is obviously necessary to have a precise knowledge of the state of the system under consideration, e.g. its electronic, vibronic, and rotational state. For small molecules, especially for dimers, this information is generally available [1],

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thus enabling an unambiguous comparison between theory and experiment. In the framework of cluster physics the situation is usually more difficult for several reasons. The most obvious problem is the lack of structural information from experiment and the incredibly large number of possible low-energy local minima on the Born–Oppenheimer surface of a cluster existing even for moderate cluster sizes. In some special cases, e.g. rare gas clusters, the occurrence of "magic numbers" for the relative stability gives some indication of the growth pattern. But even then care must be taken because of the thermodynamic properties of clusters [2,3] that are completely different from the bulk. For clusters it might be possible that several phases coexist within a finite temperature and pressure interval [2]. It is therefore of utmost importance to study the interrelations between structural and electronic properties. Although there have been attempts to understand the behavior of clusters on the basis of jellium-type models (which do not take into account any detailed information on the arrangement of the nuclei) these models do not seem to be applicable in the case of localized electrons. This holds in particular for clusters that undergo a change of the type of bonding with increasing cluster size because such changes are related to the degree of localization of the electrons [4]. A prominent example are the clusters of divalent elements from groups 2 and 12. These clusters undergo a transition from van der Waals to covalent and finally to a metallic type of bonding with increasing cluster size [5].

In the following we illustrate some of the issues mentioned above for negatively charged mercury clusters. Because of their interesting properties mercury clusters have attracted considerable attention both from theory and experiment (a detailed list of references can be found in [4]). Despite their seemingly simple electronic structure, mercury clusters present severe difficulties for *ab initio* methods. The subtle interplay between van der Waals and covalent types of bonding requires highly accurate calculations, using methods that can describe equally well both kinds of bonding [6]. For structural studies at even finite temperature the most appropriate methods seem to be simulated annealing techniques or molecular dynamics simulations using density functional theory for the electronic structure calculations. For van der Waals type of interactions the conventional density functionals do not give satisfactory results (see e.g. [7,8] for the case of Hg_2). Either they strongly overestimate the binding energy or they lead to no binding at all. This limits their usefulness, at least for small and medium sized mercury clusters, considerably. We therefore favor wavefunction-based methods like the coupled-cluster (CC) theory and the quantum Monte Carlo (QMC) techniques for our calculation of small and medium sized mercury clusters. In order to estimate the accuracy of our methods we have performed calibration calculations for the mercury dimer [6,9,10], for which we obtained very good agreement with experimental data [11]. However, these methods require a significantly larger computational effort which, with the resources presently at hand, limits our possibilities with respect to global structure optimizations.

In order to overcome this limitation we have tried to find a more approximate method that still gives reasonable structures, cohesive energies, and electron affinities. Even if such a method causes doubts concerning its reliability it can be very useful within a limited framework if it is sensibly applied. For this it is necessary to specify their range of applications by other well-established methods like those mentioned above. Recently [12], we have proposed a hybrid model (HM) method for neutral mercury clusters that fits into such a scheme. Within the HM method the effects of electron correlation are taken into account by pairwise model potentials that describe the dispersion interaction between mercury atoms. We found an excellent agreement of the structures and cohesive energies obtained from the HM model with CC and QMC calculations for small and medium sized clusters. In this article we present an extension of this method to negatively charged mercury clusters. Numerical evidence is given by comparison with CC calculations. This method makes it possible to extend the present work to larger clusters, improving our insight into the structure of these clusters.

2. Electron affinities of mercury clusters

The electronic structure of mercury clusters can be easily visualized qualitatively in terms of the linear combination of atomic orbitals (LCAO) approach, i.e. an effective one-electron picture. The valence orbital space of a mercury atom is characterized by a doubly occupied $6s^2$ shell and an empty $6p$ shell. For small clusters the atomic $6s$ orbitals combine to s-type cluster orbitals that are well separated from the corresponding p-type orbitals. All s-type orbitals are doubly occupied and the binding between the atoms is dominated by van der Waals type interactions. With increasing cluster size the gap between s- and p-type orbitals shrinks, resulting in an admixture of p-type orbitals to the occupied s-type orbitals. This is equivalent to an increasing covalent character of bonding that finally becomes metallic as the gap vanishes. Therefore, the gap in the orbital energies provides a qualitative measure for the type of bonding in a cluster. In order to get a quantitative measure it is necessary to go beyond the orbital picture and to define the gap in terms of physically well-defined quantities, i.e. quantum mechanical observables. An obvious possibility is to take the difference between the vertical ionization potential and the electron affinity of neutral clusters [13] that corresponds to the definition of the band gap in condensed matter physics.

In a recent publication, Busani et al. [14] report binding energies of the excess electron in negatively charged mercury clusters in the size range of Hg_3^- to Hg_{250}^-. They measured the binding energy of an electron in the p-type [BE(p)] and highest s-type [BE(s)] orbital using photoelectron spectroscopy. Because of the high energy of irradiated photons compared to the binding energy, this corresponds to vertical ionizations of the negatively charged clusters. It has been argued that the difference between these energies is directly related to the excitation energy of an electron from the highest occupied to the lowest unoccupied orbital in the neutral cluster, thus providing an alternative definition for the gap that might be more appropriate for finite systems. The underlying basic assumption stressed by Busani et al. in their article is that the structure of neutral and negatively charged clusters are similar. An important result of their work is that the closure of the gap occurs around Hg_{400}, an estimate that is considerably larger than the previous estimates appearing in literature [15,16].

In the present work we examine the assumption of similar structures of neutral and negatively charged mercury clusters using *ab initio* quantum chemical methods, extending the previous work of our group on mercury clusters [4,12,13]. We have used the coupled cluster method, including all single and double excitations and a pertubative treatment of triple excitations [CCSD(T)], as implemented in the MOLPRO *ab initio* program package [17]. Only the $6s$ valence electrons were treated explicitly; the core electrons have been replaced by an energy-consistent relativistic pseudopotential [18]. In order to take into account the polarization of the $5d$ shell we have added a semiclassical core-polarization potential [18]. The corresponding valence basis sets range from $(6s6p5d3f1g)$ to $(6s6p3d1f)$ depending on the cluster size. For technical details concerning the pseudopotential, core-polarization potential, and basis sets we refer to [13,18]. Because of the high computational expense of the methods applied here we were limited to small clusters with up to seven atoms. As an alternative we have used the QMC method [12,13] that achieves an accuracy comparable to the CCSD(T) method. Because we are mainly concerned with structure optimizations CCSD(T) is more appropriate in the present application and we only refer to QMC results taken from our previous publications.

It is an immediate consequence of the basic assumption that the vertical electron affinity (EA) of the neutral cluster must be in agreement with the BE(p) in the negatively charged cluster. In Fig. 1 we have plotted the EAs for Hg_3 to Hg_{13} corresponding to the most stable neutral structures from our previous publications [4,12,13] and the BE(p) measured in experiment. A direct comparison of the EA and the experimental BE(p) of [13] show rather large discrepancies between 0.4 and 0.8 eV. The calculated EAs are roughly 50% lower than the BE(p) values measured in experiment. Along with the onset of the icosahedral growth pattern at Hg_7 based on capped

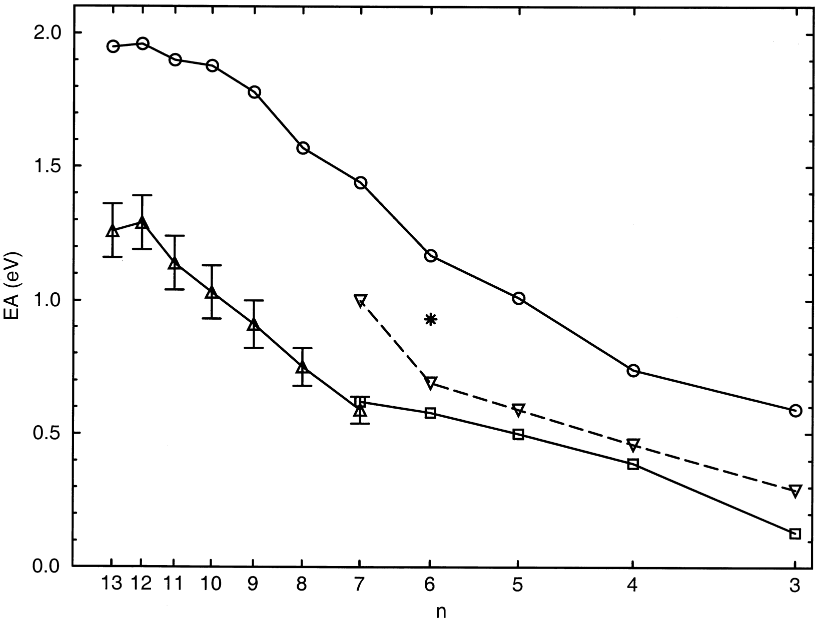

Fig. 1. Vertical electron affinities (EA) for the most stable neutral mercury clusters from CCSD(T) (squares) and QMC (triangles) calculations and binding energies of p-type excess electrons [BE(p)] for negatively charged clusters from CCSD(T) calculations (triangles indicate the same type of structures as for the most stable neutral clusters; asterisks are the most stable structure for the negatively charged cluster) and experiment (circles). The clusters are plotted over $n^{-1/3}$.

pentagonal bipyramides, we observe a change in the slope of the EA. In order to calculate BE(p) for negatively charged clusters we first had to optimize their structures. The most stable neutral clusters correspond to equilateral triangular (D_{3h}), tetrahedral (T_d), trigonal bipyramidal (D_{3h}), bicapped tetrahedral (C_{2v}), and pentagonal bipyramidal (D_{5h}) structures for Hg_3 to Hg_7. We reoptimized these structures in the presence of an excess electron. Depending on the structure we observed bond length contractions in the range of 0.02 to 0.35 Å. The details are listed in Table 1. The bond length contraction is caused by the bonding character of the p-type orbital occupied by the excess electron. The energy gain due to structural optimization is between 0.04 and 0.20 eV.

In Table 2 we list the corresponding BE(p) values for these cluster anions, which were found to be from 0.1 to 0.4 eV larger than the EA of the neutral

Table 1

Structural parameters for negatively charged mercury clusters Hg_n^-. The distances R_i [equatorial (eq), axial (ax), base (b), edge (e), surface (s)] and their changes ΔR_i with respect to the structures of the neutral clusters are given in Ångstr≠m, the corresponding relaxation energy ΔE_{opt} in electron volts

n	Structure	R_1	R_2	ΔR_1	ΔR_2	ΔE_{opt}
3	D_{3h}	3.15		0.36		0.088
4	T_d	3.21		0.14		0.035
5	D_{3h}	3.23 (eq)	3.25 (ax)	0.02	0.19	0.037
	C_{4v}	3.33 (b)	3.18 (e)	0.17	0.24	0.059
6	O_h	3.30		0.22		0.094
	C_{2v}	3.30 (s)	3.33 (e)	0.22	0.06	0.060
7	D_{5h}	3.19 (eq)	3.32 (ax)	0.35	0.09	0.201
	capped–O_h	3.26 (s)	3.31 (e)	0.17	0.13	0.074

Table 2
Calculated vertical electron affinities (EA) of neutral mercury clusters and binding energies of p-type electrons [BE(p)$_{theor}$] for negatively charged clusters. The theoretical results are compared to the experimental values BE(p)$_{exp}$. The differences between the calculated EA and BE(p) values (ΔEA) as well as between the calculated and experimental BE(p) values [ΔBE(p)] are also given. All values in electron volts

n	Structure	EA	BE$(p)_{theor}$	ΔEA	BE$(p)_{exp}$	ΔBE(p)
3	D_{3h}	0.13	0.29	0.16	0.59	0.30
4	T_d	0.39	0.46	0.07	0.74	0.28
5	D_{3h}	0.50	0.59	0.09	1.01	0.42
	C_{4v}	0.38	0.71	0.33		0.30
6	O_h	0.77	0.93	0.16	1.17	0.24
	C_{2v}	0.58	0.69	0.11		0.48
7	D_{5h}	0.62	1.00	0.38	1.44	0.44
	capped–O_h	0.84	0.96	0.12		0.48

clusters. It can be seen from Fig. 1 that although the agreement has been improved, there are still considerable discrepancies of 0.2 to 0.4 eV between theory and experiment. A series of test calculations (with and without accounting for spin-orbit interaction for selected clusters) revealed that spin-orbit contributions are less than 0.1 eV and therefore not responsible for the disagreement. It must be mentioned, however, that for the neutral clusters alternative structures exist that are only slightly higher in energy than the structures mentioned above. We have therefore extended our study to a pyramidal (C_{4v}), octahedral (O_h), and capped octahedral (*capped*–O_h) structure for Hg_5^-, Hg_6^-, and Hg_7^-, respectively. It already appears that for the neutral structures the anions of the O_h and *capped*–O_h structures are more stable than those of the C_{2v} and D_{5h} structures for Hg_6^- and Hg_7^-, respectively. The relative energies of these negatively charged clusters are listed in Table 3. It can be seen that the relative energies remain almost unchanged through the optimization for Hg_5^- and Hg_6^-, whereas the effect is more severe for Hg_7^- when the D_{5h} structure becomes the most stable. For Hg_6 it actually appears that the neutral and negatively charged cluster exist in different structures. The relatively large effect of the optimization on the BE(p) for Hg_7^- offers a possibility to resolve the relatively large discrepancy of ≈0.8 eV between the calculated EA and experimental BE(p) for the larger clusters between Hg_8^- and Hg_{13}^- (see Fig. 1). The underlying building block in all of these cases is a pentagonal bipyramid [12]. In the case of optimization effects comparable to Hg_7^-, the overall agreement would become similar to the small clusters. For Hg_5^- the D_{3h} structure remains more stable than the C_{4v} structure, however, the energy difference is only 0.05 eV, which opens the possibility that for hot clusters both structures coexist. A similar situations appears for Hg_7^-, where the energy difference between the D_{5h} and *capped*–O_h structure is 0.05 eV. In this context it should be mentioned that the “peaks” in the photoelectron spectra actually extend over approximately 0.6 to 0.8 eV (see Fig. 2 in [14]). The experimental BE(p) were assigned to the center of the signal with estimated error bars of 0.15

Table 3
Relative stabilities of various structures of small mercury cluster anions Hg_n^-. The first given structure is the more stable one after optimization. All values in electron volts

		Structure optimized for	
n	Structure	Hg_n	Hg_n^-
5	$D_{3h} - C_{4v}$	0.077	0.054
6	$O_h - C_{2v}$	0.100	0.134
7	D_{5h} − *capped*–O_h	−0.073	0.054

Table 4
Calculated binding energies of s-type electrons [BE(s)] for negatively charged mercury clusters in comparison to the experimental values (exp). The differences between the calculated and experimental values [ΔBE(s)] are also given. All values in electron volts

n	Structure	$\mathrm{BE}(s)_{theor}$	$\mathrm{BE}(s)_{exp}$	ΔBE(s)
3	D_{3h}	4.30	4.02	0.28
4	T_d	4.65	3.90	0.75
5	D_{3h}	4.38	3.92	0.46
	C_{4v}	3.96		0.04
6	O_h	4.10	3.92	0.18
	C_{2v}	4.38		0.46
7	D_{5h}	4.35	4.05	0.30
	capped–O_h	4.20		0.15

eV. Comparing our calculated BE(p) with the photoelectron spectra we find that for all cases our results are well within the width of the "peaks."

Beside the binding energy of an electron in the singly occupied p-type orbital, Busani et al. [14] also measured the binding energy of electrons in the highest s-type orbital BE(s). This property is also accessible to calculations and has been determined for the optimized structures of the negatively charged clusters. Our results are in fairly good agreement with experiment, as can be seen from Table 4. For Hg_3^-, Hg_6^-, and Hg_7^- the discrepancies are below 0.3 eV. For Hg_5^- we found that the BE(s) of the slightly less stable C_{4v} structure is in very good agreement with experiment, whereas for the D_{3h} structure the calculated BE(s) is too large by almost 0.5 eV. As mentioned above, it might be possible that for hot clusters both species coexist. For Hg_4^- the discrepancy is especially large, i.e. almost 0.8 eV. The reason behind this discrepancy has so far not been resolved.

3. An extension of the hybrid model method to negatively charged clusters

The HM method proposed for the approximate treatment of electron correlation effects on the structures and cohesive energies of neutral mercury clusters consists of a pairwise additive effective dispersion potential added to the HF energy.

$$E(\mathrm{Hg}_n) = E_{HF}(\mathrm{Hg}_n) - \sum_{i<j}^{n} \frac{C_6 f_6(R_{ij})}{R_{ij}^6} \tag{1}$$

The correlation potential contains the leading $1/R^6$ contribution to the dispersion interaction and a cutoff function

$$f_6(R) = [1 - \exp(-\alpha R^2)]^3 \tag{2}$$

that suppresses the dispersion term in the region where the core–core repulsion becomes dominant and removes the singularity at the origin. The underlying physical assumption is that the covalent contributions are already present at the HF level and the electron correlation contributions are dominated by dispersion type interactions. Dispersion interactions do not contribute to charge fluctuations between atomic domains. Therefore, our assumption has been checked by analysing the effect of correlation on atomic charge fluctuations. This has been done using QMC techniques; we refer to [12] for further details. Presuming that the dispersion interactions between the atomic $6s^2$ shells do not change in going from the neutral to the negatively charged clusters, it is only necessary to add the correlation contributions caused by the excess electron. Here we assume the additivity of different correlation contributions that should be fulfilled within a reasonable approximation. In order to extend the HM method to negatively charged clusters we have therefore performed configuration interaction calculations taking into account single and double excitations (SDCI) where the double excitations were restricted from those orbital pairs that contain the orbital occupied by the excess electron. Obviously this reduces the computational effort considerably, compared to a complete SDCI or even

Table 5
Structural parameters and BE(p) for negatively charged mercury clusters Hg_n^- calculated with the extended HM methods. The distances R_i and their deviations ΔR_i from CCSD(T) calculations are given in Ångstrøm, the corresponding BE(p) and their deviation ΔBE(p) from CCSD(T) calculations are given in electron volts

n	Structure	R_1	R_2	ΔR_1	ΔR_2	BE(p)	ΔBE(p)
3	D_{3h}	3.17		0.02		0.36	0.07
4	T_d	3.21		0.00		0.55	0.09
5	D_{3h}	3.28 (eq)	3.27 (ax)	0.05	0.02	0.70	0.11
6	O_h	3.32		0.02		1.06	0.13

CCSD(T) calculation. We have used the MOLPRO program package [17] to perform such calculations. The energy of a negatively charged cluster is therefore given by

$$E(Hg_n^-) = E_{SDCI}^{excess}(Hg_n^-) - \sum_{i<j}^{n} \frac{C_6 f_6(R_{ij})}{R_{ij}^6} \tag{3}$$

and the BE(p) can be obtained from $E_{HF}(Hg_n) - E_{SDCI}^{excess}(Hg_n^-)$.

Using the extended HM method we have optimized the structures of selected negatively charged clusters. The results for Hg_3^-, Hg_4^-, Hg_5^- (D_{3h}), and Hg_6^- (O_h) are listed in Table 5. It can be seen that the bond lengths are in very good agreement with the CCSD(T) calculations mentioned above. They are slightly too long by ≈0.02 Å. The BE(p) are overestimated by 0.07 to 0.13 eV, which seems to be acceptable, in view of the approximations involved. The extended HM method provides a tool for studying the structures of considerably larger clusters than have been studied until now. More work must be done in order to investigate its range of applications.

4. Conclusions

The aim of our article is to show that there are subtle relationships between the structure and electronic properties of negatively charged mercury clusters. This complicates a direct comparison between theory and experiment, but at the same time opens the possibility for extracting structural information from experimental data. In order to put such reasoning on firm ground it is necessary, however, to examine finite temperature effects on the structure of clusters. We obtained significant structural changes by optimizing the structure of negatively charged clusters, which resulted in notable differences between the calculated EA and BE(p). Because of the limitations of our calculations to relatively small clusters it might be premature to draw far reaching conclusions concerning similar effects for larger clusters. In particular, the relatively large effect for Hg_7^- indicates a promising perspective for the clusters between Hg_8^- and Hg_{13}^-. We want to mention, however, that in our recent study of neutral clusters [12], use of the HM method in the range from Hg_7 to Hg_{13} revealed several possible candidates (like capped prisms) that were only slightly less stable than the *capped*–D_{5h} structures found to be the most stable. The situation might therefore become rather complicated within this range of cluster sizes. It is left for future studies to apply computationally simpler methods like a modified HM method to a larger variety of possible structures of negatively charged clusters in order to find the most stable ones.

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