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Cohesive properties of mercury clusters in the ground and excited states

H. Kitamura[a]

Department of Physics, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

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Abstract. Optimized structures and cohesive energies of small mercury clusters (Hg$_N$; N = 3–7, 13, 19) are calculated with the spin-orbit diatomics-in-molecules method. The theory takes into account the effect of *s*-*p* mixing which tends to enhance the binding energies in the ground state. It is shown that excimer clusters have significantly short optimum bond lengths and their atomic geometries differ considerably from those in the ground state. Excitation energy gap depends sensitively on both cluster size and nearest-neighbor separation. Numerical results are compared with other theories and experiments.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 36.40.-c Atomic and molecular clusters

1 Introduction

Mechanisms of vapor-liquid and metal-nonmetal transitions in expanded fluid mercury have been long-standing issues in physical chemistry [1]. It is not trivial to identify the microscopic origin of attractive interatomic interactions responsible for the transitions, because the binding energy (about 0.043 eV) of a Hg$_2$ molecule in the ground X0_g^+ state [2], which consists of two closed-shell atoms in the $6s^2$ ^{1}S$_0$ configuration, is too small to account for the observed critical temperature (0.151 eV) of bulk mercury [1]. It is therefore essential to find out how strong cohesive forces may arise when several atoms associate to form clusters.

Recently, diatomic potential energy curves (PECs) of mercury have been studied in detail for both ground and low-lying excited states by means of ab initio quantum-chemical computations [2,3] and spectroscopic measurements [4]. Figure 1 exhibits the ab initio ground-state PEC by Schwerdtfeger et al. [2] based on spin-orbit-corrected scalar relativistic coupled-cluster calculations with large uncontracted ($11s10p9d4f3g2h$) basis set, and excited-state PECs by Czuchaj et al. [3] based on SCF and MRCI scheme with ab initio quasi-relativistic energy-adjusted pseudopotentials for the core electrons. In contrast to the ground-state PEC dominated by repulsion, strong attractive forces in excited-dimer PECs are remarkable. This immediately suggests that admixture of excited states into the ground state would produce strong binding force in clusters.

In this paper, we develop a theoretical framework for constructing potential energy surfaces of Hg$_N$ clusters by combining the known atomic energy levels and diatomic PECs, and thereby investigate their cohesive properties.

2 DIM calculations of Hg$_\mathrm{N}$ clusters

Our theory is based on the spin-orbit diatomics-in-molecules (DIM) method [5] with configuration mixing, as reported elsewhere [6,7]. We use ab initio diatomic PECs shown in Figure 1. Spin-orbit interaction is treated as superposition of individual atomic contributions. The electronic state of a Hg$_N$ cluster is described by a linear combination of polyatomic basis functions (PBFs); each PBF is a product of localized atomic wavefunctions $|LSM_LM_S\rangle$. The ground-state PBF is given simply as $|0\rangle \equiv \overset{1}{|0000\rangle} \cdots \overset{N}{|0000\rangle}$, which means that all the atoms are in the ground $6s^2$ ^{1}S state. We likewise introduce excited-state PBFs of the form, $|k; SM_LM_S\rangle \equiv \overset{1}{|0000\rangle} \cdots \overset{k}{|1SM_LM_S\rangle} \cdots \overset{N}{|0000\rangle}$ ($k = 1, ..., N$; $S = 1, 0$; $M_L = 1, 0, -1$; $M_S = S, S-1, ..., -S$), where kth atom is in the excited $6s6p$ $^{2S+1}$P state. Overlap of these wave functions is neglected for simplicity.

The cluster Hamiltonian is decomposed into diatomic fragments [5], whose matrix elements are evaluated in terms of the corresponding diatomic PECs. Directional dependence of chemical bonding is naturally taken into account through transformation of the wavefunctions from diatomic to laboratory frame. In each diatomic fragment,

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[a] e-mail: `kitamura@scphys.kyoto-u.ac.jp`

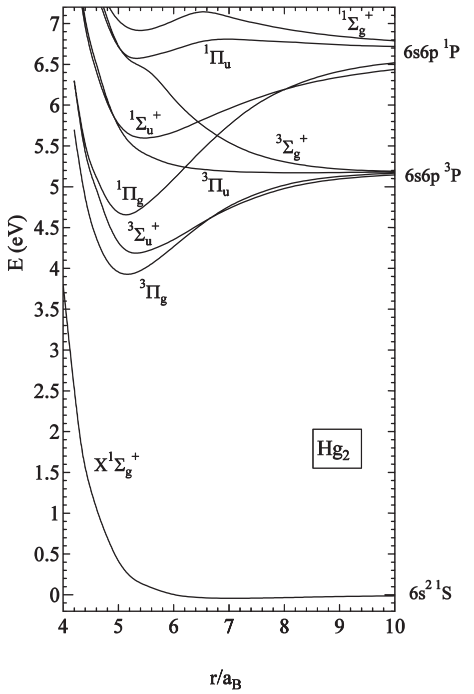

Fig. 1. Ab initio potential energy curves of Hg$_2$ in the ground state [2] and low-lying excited states [3].

s-p mixing arises as a result of configuration interaction between ground and excited states of the same $^1\Sigma_g$ symmetry; the mixing parameters depend on the interatomic distance, and their functional forms have been determined through a variational procedure within the empirical valence-bond theory [7]. Diagonalization of the Hamiltonian matrix yields energy eigenvalues and eigenfunctions for the ground and excited states of the cluster.

2.1 Ground state

Optimized atomic geometries of Hg$_N$ clusters in the ground state turn out to be equilateral triangle (D$_{3h}$) for $N = 3$, tetrahedron (T_d) for $N = 4$, trigonal bipyramid (D$_{3h}$) for $N = 5$, octahedron (O$_h$) for $N = 6$, and pentagonal bipyramid (D$_{5h}$) for $N = 7$, respectively [6]. These are close packed structures characteristic of van der Waals clusters constructed from closed-shell atoms [8]. For $N = 13$ and $N = 19$, icosahedral (I$_h$) and double icosahedral (D$_{5h}$) structures are found to be the most stable.

Static ground-state energies of these clusters are plotted in Figure 2, where energy of the ground Hg(^{1}S$_0$) state is taken as zero. When s-p mixing is neglected, the ground-state wavefunction coincides with the ground-state PBF, $|0\rangle$, and the corresponding energy is given simply by summation of ground-state diatomic PECs over all pairs of atoms. It is shown that s-p mixing tends to enhance the binding energies substantially over those expected from binary forces alone.

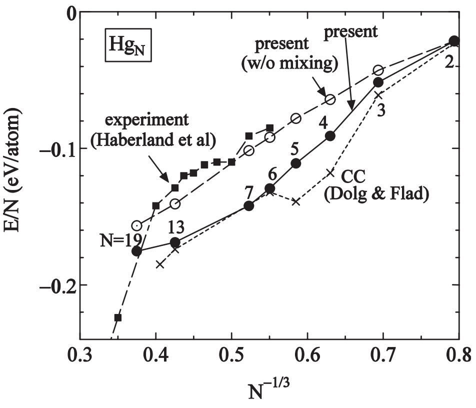

Fig. 2. Static ground-state energies (per atom) of Hg$_N$ clusters. The solid line accounts for s-p mixing; the dashed line neglects s-p mixing. The results are compared with coupled cluster (CC) calculations by Dolg and Flad [9] and experimental data by Haberland et al. [10].

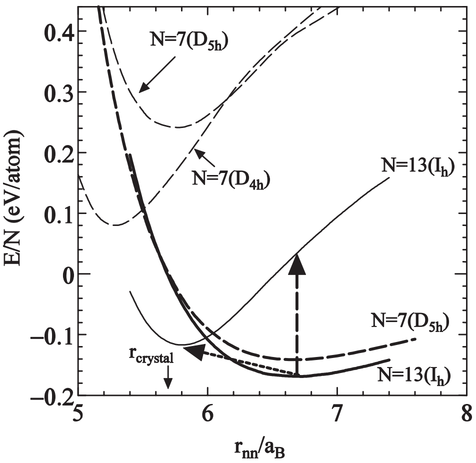

Fig. 3. Comparison of the energies per atom of Hg$_7$ and Hg$_{13}$ clusters in the ground state and the first excited state as functions of the nearest-neighbor interatomic distance.

In Figure 3, the potential energy surfaces of Hg$_7$ and Hg$_{13}$ clusters are indicated by thick dashed and solid curves, respectively, as functions of the nearest-neighbor distance, r_{nn}. We find that the equilibrium bond lengths of the clusters are shorter than the corresponding value, $7.07a_B$, of the ground-state dimer, where a_B denotes the Bohr radius. Such bond contraction is also the consequence of s-p mixing.

We find in Figure 2 that the present DIM results agree fairly well with the ab initio CCSD(T) calculations by Dolg and Flad [9]. The experimental values by Haberland et al. [10] are somewhat larger for $N < 13$, but decrease steeply as N increases further; these authors argue that s-p hybridization becomes so strong that the clusters with N = 30–70 are dominated by covalent bonding. In the present theory, however, hybridization effect for $N = 19$ is weaker than that for $N = 13$, as indicated by the difference between solid and dashed curves in Figure 2. Accurate evaluation of cohesive energies for larger clusters may require larger basis sets including simultaneous excitation of two atoms or charge-transfer excited states.

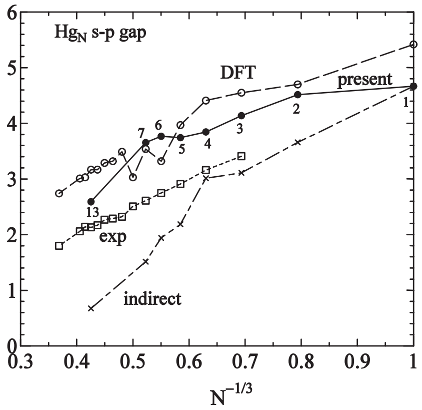

Fig. 4. Vertical energy gap of Hg_N clusters calculated for optimized geometries in the ground state, compared with density functional theory (DFT) [12] and experimental (exp) [13] results. For comparison, indirect energy gap in this work is also plotted.

2.2 Lowest excited state

We have likewise analyzed stable geometries for the lowest excited state. For $N \leqslant 4$, we predict the same close-packed structures as the ground-state clusters. In contrast, for $5 \leqslant N \leqslant 7$, we have obtained peculiar cluster geometries such as D_{4h} and C_{4v} characterized by bond angle of 90° [6]. The corresponding nearest-neighbor bond lengths are found to be significantly small compared with the ground-state clusters. For illustration, the potential energy surface of an excited Hg_7 cluster in the D_{4h} configuration is exhibited in Figure 3; it turns out that the optimum bond length is as small as $5.28a_B$. The excimer clusters are compact and tightly bound owing to the strong attractive $\mathrm{Hg}(^1\mathrm{S})$-$\mathrm{Hg}(^{1,3}\mathrm{P})$ interactions as we observe in Figure 1 [3]. Analysis of the wavefunctions reveals that the central atom has a predominant p-character, strongly attracting the surrounding six atoms which are dominated by s-characters.

We find that the optimized geometry of Hg_{13} is icosahedron (I_h) for both the ground and excited states. We demonstrate in Figure 3 the corresponding potential energy surfaces. The equilibrium bond length in the ground state amounts to $r_{nn} = 6.67a_B$, whereas the corresponding value in the lowest excited state is $5.80a_B$; we note that this latter value is close to the nearest-neighbor distance, $r_{crystal} = 5.68a_B$, in the rhombohedral lattice of metallic crystalline mercury near the freezing point [11].

It is notable that the "indirect" energy gap between the potential minima of the ground and excited states, shown by the dotted arrow in Figure 3, is considerably smaller than the Franck-Condon vertical energy gap depicted by the dashed arrow. Figure 4 summarizes the size dependence of vertical and indirect energy gaps. Our vertical gap compares well with the density functional theory (DFT) by Moyano et al. [12]. The experimental data by Busani et al. [13] are based on photoelectron spectra of Hg_N^- clusters. The indirect energy gap decreases rapidly with increasing N, while vertical energy gap decreases rather gradually [12,13].

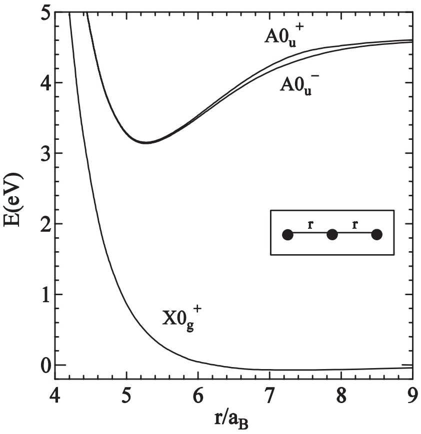

Fig. 5. Potential energy surfaces of linear symmetric trimers relevant to the blue-green emission.

2.3 Blue-green emission from Hg_3

A broad continuum emission centered at 485 nm, observed in optically excited mercury vapor [14], has been known for a long time as the blue-green emission. Experimentalists have speculated that it may originate from excited Hg_3 [14,15]. The first theoretical assignment was given by Omary et al. [16] through coupled-cluster calculation, which treats $5d$ electrons explicitly as valence states; they attributed the blue-green emission to the $^3\Pi_u$ state of linear symmetric Hg_3. Spin-orbit interactions were neglected there, however.

As we show in Figure 5, the present spin-orbit DIM calculation predicts that the excited $\mathrm{A}0_u^+$ state of a linear symmetric Hg_3 cluster, which is located at 3.15 eV with $r_{nn} = 5.27a_B$ [7], undergoes a radiative decay to a dissociative ground state via emission of 462 nm; this value is in reasonable agreement with the observed wavelength of the blue-green emission, judging from the broad nature of the spectrum [14]. Our theory thus corroborates the earlier conjecture by Callear [15], namely, $\mathrm{Hg}_3(\mathrm{A}0_u^+) \rightarrow 3\mathrm{Hg}(6^1\mathrm{S}_0) + h\nu(485\ \mathrm{nm})$.

3 Concluding remarks

By using the DIM theory, we have analyzed potential energy surfaces for both the ground and excited states of small mercury clusters by incorporating ab initio diatomic potential energy curves and spin-orbit interactions. Ground-state clusters have close-packed optimum geometries, and their binding energies take on enhanced values due to many-body interactions stemming from s-p mixing. On the other hand, the clusters in the lowest excited states have considerably smaller equilibrium bond lengths, reflecting the properties of tightly bound excited dimers. As a consequence of such structural difference, vertical excitation energy gap is rather large and decreases gradually with increasing cluster size [12,13], while indirect energy gap is much smaller than the vertical gap; the latter feature has not necessarily been discussed in previous investigations.

The fact that excitation energy gap depends sensitively on the interatomic separation implies the presence of spatially inhomogeneous energy gap in fluid mercury associated with local density fluctuation [17]. Also, many-body forces due to *s*-*p* mixing would be essential for predicting macroscopic thermodynamic behavior of fluid mercury near the critical point [18] as well as solid mercury at low temperatures [11]. In future, extension of the present work to larger clusters is highly desirable, but larger basis sets would be required to describe strong covalent bonding and metallization.

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