

Ground state and response properties of mercury clusters

Hellmut Haberland, Bernd von Issendorff, Ji Yufeng [*], Thomas Kolar, and Gregor Thanner

Fakultät für Physik,
Universität Freiburg, H.Herderstr. 3, D7800 Freiburg, Germany

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Abstract. The change of the cohesive energy and the optical absorption spectra of small singly sized Hg clusters is discussed. The cohesive energy allows one to determine the different regimes of chemical bonding. The optical spectra show an abrupt transition to a collective, plasmon-like absorption as a function of increasing cluster size. The position of the one plasmon peak is: 1) independent of the charge state, 2) nearly independent of cluster size, and 3) agrees with that of the classical Mie plasmon calculated from the experimental dielectric constants. The width of the plasmon peaks is discussed. A strong influence of electronic correlations on the cluster size dependence of the oscillator strength is observed.

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1) Introduction

The Hg atom has a $5d^{10}6s^2$ closed shell electronic structure. It is thus isoelectronic to $\text{He}(1s^2)$. Because of the closed shell structure it is dominantly van der Waals bound for the diatomic molecule and small clusters. The bands derived from the atomic $6s$ and $6p$ bands broaden with increasing cluster size, as indicated in fig. 1, but a finite gap Δ remains. The binding is covalent, as in a semi-conductor with decreasing bandgap. At some cluster size the gap becomes so small, that the binding is effectively metallic. One has thus an “isolator to metal” transition as a function of cluster size.

Several groups have studied this transition in chemical bonding. The earliest theoretical study goes back to a 1943 paper by Landau and Zeldovich [1]. Renewed interest came from the experimental [2], and theoretical [3] studies of “expanded mercury”, where the bulk proper-

ties of Hg were studied at high pressure and temperature. Cabaud et al. were the first to study properties of free clusters [4]. Rademann et al. measured photoionization processes [5]. The excitation of the $5d \rightarrow 6p$ autoionizing transition was probed by Bréchnac et al. [6]. Dissociation and cohesive energies, as well as ionization energies were measured by this group [7, 8] and calculated by Bennemann et al. [9].

The following picture has emerged from these studies. For $n \leq 20$ the binding is dominantly van der Waals. The bandgap [10] Δ is so large, that sp hybridization is energetically not favoured. Experiment and theory agree that the cohesive energy scales as expected for a Lennard-Jones cluster. After a transition region the bonding becomes covalent ($n \geq 30$). The bandgap decreases, thus increasing the importance of sp hybridization, which leads to an increase in bonding between the atoms. There is still some dispute, on where the overlap of the s and p bands becomes complete. Rademann [5] deduces from

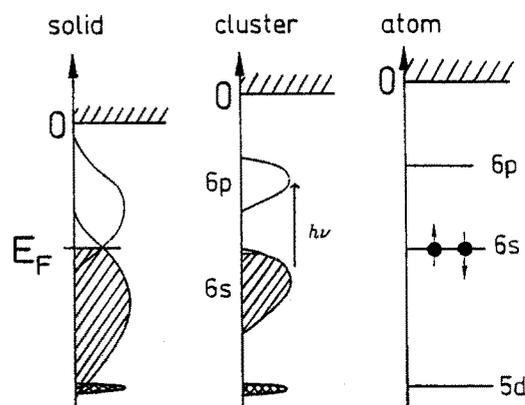


Fig.1 Electronic structure of the Hg atom, cluster, and bulk. For sufficiently large clusters the sp -band overlap leads to metallic behaviour. Thus an isolator to metal transition occurs as a function of cluster size.

his data $n \approx 70$, Pastor et al. [11] calculate $\Delta(n = 135) \leq 100$ meV. Unpublished data from this group point to even larger values [8].

2) Cohesive energy

The cohesive energy E_{coh} is by definition the total binding energy per atom. One can write:

$$E_{coh}(n) = \frac{1}{n} \sum_{i=2}^n D_0(n) \quad (1)$$

where $D_0(n)$ is the dissociation energy of a cluster of n atoms. The dissociation energies of the charged clusters $D_0^+(n)$ have been determined earlier from an analysis of the metastable decay of mass selected Hg_n^+ [7, 12]. The dissociation energies of the neutral clusters can be calculated from a Born-Haber cycle, provided the ionization energies are known [7]. The cohesive energies can then be calculated from eq. 1. The black dots in fig. 2 show the results obtained in this way. The newest theoretical result [9] agrees quantitatively with the experimental curve for neutral clusters up to $n = 21$, and qualitatively up to $n = 43$. The open circles joined by the dashed line marked "van der Waals" show the cohesive energies calculated for icosahedral clusters bound by a Lennard-Jones potential [13], which was scaled to the binding energy of Hg_2 ($E_{coh}(2) = D_0(2)/2 = 21 \pm 2$ meV) [14]. For cluster sizes up to $n = 21$ the calculated and experimentally determined cohesive energies agree with the calculations for Lennard-Jones clusters. This coincidence leads to the claim that small Hg_n , $n \leq 21$ are van der Waals bound. One can raise theoretical arguments against this classification, as already the wavefunction for Hg_2 has components which

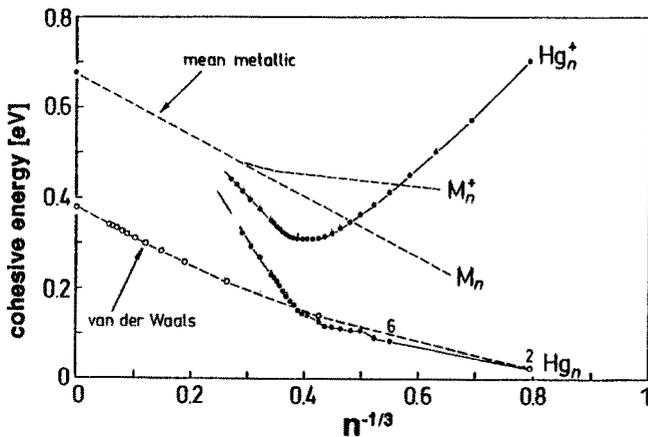


Fig. 2 Cohesive energies for neutral and ionized clusters (solid points). See text for details. Up to $n = 21$ the experimental results follow the curve expected for a van der Waals like behaviour. This is in agreement with the latest calculations. For larger n a slow transition to the values expected for metallic behaviour is seen.

are far from van der Waals like [15]. But the classification remains useful, as the van der Waals contribution seems to dominate at least up to $n = 21$.

The dissociation energy of the dimer ion, Hg_2^+ , is a factor of about 30 larger than that of the neutral dimer. A similar behaviour is found for the rare gases. In both cases an electron from a strongly antibonding σ_u orbital is ejected, leading to the large increase in binding energy. The same effect is responsible for charge localization in small rare gas clusters [16]. Xe_n^+ has an electronic structure like $(\text{Xe}_i^+) \text{Xe}_{n-i}$, with $i = 3$ or 4. A similar charge localization was very recently calculated for Hg_n^+ , and found to explain the observed ionization energies [17]. Thus small rare gas and mercury clusters do indeed behave similarly.

3) Optical response

The photofragmentation spectrometer has been described in detail [18]. It is an improved version of that used earlier to measure optical spectra for Ar_n^+ and Xe_n^+ clusters [16]. Briefly, an Ar seeded supersonic expansion generates the Hg clusters. They are ionized by electron impact, and a reflectron time of flight (TOF) mass spectrometer is used to separate cluster ions of different mass in time and space. Clusters of one size are irradiated by photons from an excimer pumped pulsed dye laser. The photoinduced electronic excitation is rapidly converted into vibrational energy, leading to ejection of atoms. A second TOF measures the fragment spectrum. The intensity I of the selected clusters is recorded with (I) and without (I_0) laser interaction. The photofragmentation cross section σ is calculated from $I/I_0 = (1 - \beta) + \beta \exp(-\sigma\phi)$, where the values of σ and β (geometric overlap of photon and cluster beam) are determined from measurements of I/I_0 as a function of photon fluence ϕ at one fixed wavelength. Typical values for β are 0.7 to 0.9. Note that one can obtain an absolute value for σ by measuring the photon fluence absolutely, which is easily done. It is assumed that each absorbed photon leads to ejection of at least one atom, an assumption which had been made earlier for warm clusters [19 - 25]. In this case σ is equal to the desired photoabsorption cross section. This assumption is valid for these relatively small clusters, which have been additionally heated by electron impact ionization. A short report has been published earlier [26].

Fig. 3 shows data for singly charged clusters. Sharp lines can be seen for small n , which shift [27] to the red with increasing cluster size. They could be due to transitions from the 6s to the 6p band (compare fig. 1), with some influence of the charge, as the spectra of singly and doubly charged clusters are similar but not identical. The width of both bands increases, and the band gap Δ decreases as a function of the cluster size, which makes the observed red shift plausible. A closer inspection shows that there are actually one small and one large

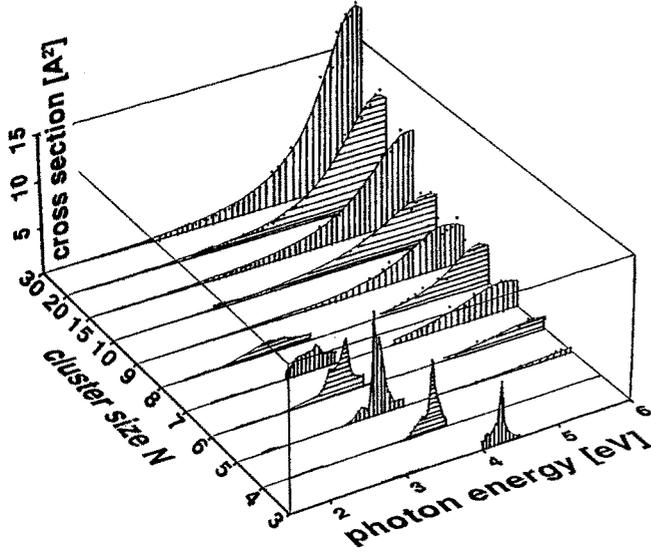


Fig.3 Photoabsorption spectra of singly charged Hg-clusters. The photo absorption cross section in Å² is plotted as a function of cluster size and photon energy. The peaks at ≥ 5 eV are interpreted as plasmon excitations.

peak, the latter consisting sometimes of 2 or 3 peaks. This will be discussed in more detail elsewhere [28]. This fine structure could possibly be the signature of highly correlated electrons [29].

At some small n ($n \geq 6$ for singly charged, and $n \geq 13$ for doubly [26] charged clusters) the intensity of the sharp lines decreases rapidly, and a broad unstructured peak appears at $\hbar\omega \geq 5.0$ eV. This peak has been identified as a collective, “plasmon” type of absorption [26]. The spectrum could only be measured up to 5.9 eV, as this is the high frequency limit of the BBO2 frequency doubling crystal used. No splitting of the plasmon peaks is observed, in contrast to the alkali case. From the analysis given in ref. [26] one can deduce the following properties: 1) The peak position of the plasmon peak ω_0 is nearly independent of cluster size down to the surprisingly small cluster size of $n = 5$. 2) The value of ω_0 agrees well with that calculated from the classical dielectric constant. 3) The influence of the 5d electrons shifts the free electron value for ω_0 from 6.1 eV to the experimentally observed $\omega_0 = 5.7$ eV. 4) The large bulk plasmon linewidth is due to the poor electric conductivity of bulk Hg at 300 K. 5) Singly and doubly charged Hg clusters have, within experimental accuracy, the same plasmon peak position.

4) Linewidth of the plasmon

The width of the plasmon resonances has been discussed earlier [26]. The relation:

$$\Gamma = \Gamma_0 + A \frac{v_F}{R}, \quad (2)$$

where Γ_0 is some intrinsic width, and v_F the Fermi velocity ($1.58 \cdot 10^6$ m/s for bulk Hg), is often used to explain the width Γ of cluster plasmon resonances [32]. A fit to this equation gives $\Gamma_0 = 0.49 \pm 0.05$ eV. The value of A depends on whether the van der Waals ($A = 0.41 \pm 0.03$) or metallic ($A = 0.37 \pm 0.02$) internuclear distance is used to calculate the cluster radius R from the number of atoms in the cluster [9]. The earliest [33] random phase approximation (RPA) jellium calculation gives $A = 0.2$, while the newest theory [34] gives $A = 0.534$ for the case of Hg. The experimental values lie between the two results.

The Hg cluster plasmon width seems to have two components: one independent of cluster size (Γ_0 , given by the Drude relaxation rate, strong temperature effect expected) and one due to “Landau damping” (second term in eq. 2, temperature independent) [33, 34]. Landau damping is a mechanism of plasmon decay, whereby it transfers its energy into excitation of a single electron. This electronic energy must then decay into vibrational excitation to be detectable by our experiment, as discussed above.

5) Oscillator strengths

The measurement of the oscillator strength will be discussed now. One needs the absolute value of the cross section in order to obtain the oscillator strength. The determination of the cross section is accurate to 10% for $\hbar\omega \leq 3.8$ eV, where the direct output of a dye laser can be used. It becomes about 20% for higher photon energies, due to the larger intensity fluctuations and lower intensity after frequency doubling. The error in the absolute cross section depends mainly on the accuracy of the laser fluence measurement.

A Drude like dielectric function [30, 31] gives for the photoabsorption cross section:

$$\sigma_n(\omega) = \sigma_n(max) \frac{\Gamma^2 \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \cdot \quad (3)$$

Here $\sigma_n(max)$ is the value of the cross-section at the maximum. The resonance frequency ω_0 and the width of the resonance Γ depend on cluster size n . This equation describes reasonably well the plasmon lineshapes of the spherical alkali [19 - 24] and silver [25] clusters. The Hg cluster plasmon maxima and that calculated from the classical dielectric function [26] were also found to be well represented by eq. 3.

The oscillator strength f is proportional to the area under the absorption lines: $f = 0.911 \int \sigma(E) dE$, where the photoabsorption cross section $\sigma(E)$ is measured in Å² and the photon energy E in electron Volts. As eq. 3 gives a good fit to the cluster plasmon peaks as well as the macroscopic Mie plasmon it was used to extrapolate the data to the sofar “unmeasurable” blue side of the plasmon. This assumption should be good: Integrating $\sigma(E)$ only up to the maximum and doubling this value

gives, within experimental error, the same result. Fig. 4 shows the results for singly charged clusters. The oscillator strength of the narrow peaks at small n is 0.18 per 6s-electron for $3 \leq n \leq 5$. It then decreases rapidly and becomes very small for $n > 10$. The plasmon starts at $n = 5$, and increases rapidly. The bulk value is 0.53, as discussed elsewhere [26]. This value is indicated by the horizontal solid line. The f -value of the $^1S \rightarrow ^1P$ transition of the *neutral* atom is 0.59, This value is given by the horizontal dashed line in fig. 4. The error bars give the statistical variation only. Thus all plasmon f values between 7 and 100 are compatible with the atomic or bulk result. The data for doubly charged clusters look similar, the only difference is that the transition from atomic to plasmon like behaviour occurs not around 10 but around $n = 20$ [26].

As soon as the plasmon absorption starts, it gets most of the oscillator strength. This is the behaviour expected for a transition from a dominant single electron to a collective, plasmon-like transition, for which the simplest theoretical treatment is given by the "schematic model" of the giant dipole resonance of nuclear physics [35, 36]: Assume one has some zero order single particle states, where particle means nucleon in nuclear physics and electron in our case. These could be obtained, e.g. in a Hartree-Fock or local density type of calculation, neglecting correlations. If correlation is increased new states are formed. One transition, which can only be described as collective, is shifted strongly in energy and gets (nearly) all the oscillator strength. The other transitions remain dominantly single particle; they shift a bit in energy and lose all their oscillator strength. This reasoning fits our data beautifully.

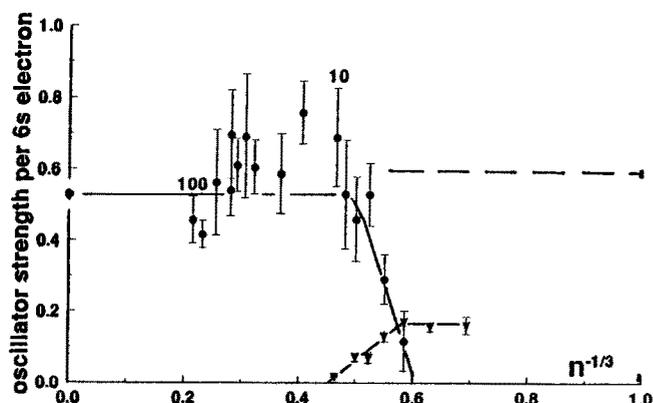


Fig. 4 The oscillator strength per 6s electron for singly charged clusters is plotted against $n^{-1/3}$. Note the abrupt transition from single particle to plasmon-like absorption. The bulk oscillator strength of the Mie plasmon is only 0.53, due to the influence of the 5d electrons.

6) Summary

In summary, cohesive energies and optical spectra of small Hg clusters have been discussed. Experiment and theory agree that the cohesive energy scales as expected for a Lennard-Jones cluster for $n \leq 21$. The optical spectra of Hg_n^+ and Hg_n^{++} show both narrow lines, which can probably be classified as $6s \rightarrow 6p$ transitions - with some influence of the charge - and broad, plasmon-like maxima. The oscillator strengths of these two different absorptions show an abrupt transition as expected for a transition from a case of weak to one of strong electronic correlation.

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