Direct Observation of Band-Gap Closure in Mercury Clusters

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We have measured the photoelectron spectra of mass-selected negatively charged mercury clusters Hg^-_n in the size range $n = 3-250$. The spectra are characterized by gaps which shrink with increasing n. These gaps represent the s-p excitation band gaps of the corresponding neutral clusters. Extrapolation to higher cluster size indicates band gap closure at the size range of $n = 400 \pm 30$, a considerably larger value than previously reported ($n = 80-100$). This new evaluation indicates that previous experimental criteria for the band closure are not appropriate and calls for a refined theoretical formulation of the electronic structure of mercury clusters. [S0031-9007(98)07409-2]

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The evolution of the metallic nature in metal-atom clusters has been a subject of interest during the last two decades [1,2]. The common wisdom is that in simple monovalent metals (such as alkali or coinage elements) the metallic nature results from the evolution of the half-filled valence-electron band states [2]. In bivalent metal, however, of the IIA and IIB groups, valence electrons form a fully occupied s^2 band and a completely vacant p band. It is plausible for such materials to be semiconductors. Several effects take place with increasing cluster size. The bandwidths increase, and the s-p band gap decreases, with corresponding increase in the s-p hybridization. At some critical cluster size these effects lead to s-p band overlap and the formation of a partially full band, an essential property for any metallic matter.

During the last decade, several experimental and theoretical studies have focused on the size dependent properties of mercury clusters [3]. The first mass-selected spectroscopic studies on inner shell excitations of mercury clusters [4] revealed a transition region from van der Waals binding to distinct covalent binding in the size range of $n = 13-20$. This observation was further supported by the plasmon excitation studies [5] and the cohesive energy studies [6] of Haberland and co-workers. For $n > 20$ a gradual change of the s-p hybridization was observed [7]. The ionization size dependence [6,8] as well as the cohesive energy was reported to approach the expected values of finite-size metallic particles. These experimental studies were accompanied by theoretical formulation of the change in the nature of the electronic states in mercury clusters, mainly by Bennemann and co-workers [3,9]. All of the experimental as well as the theoretical studies imply that s-p band merging occurs at the size range $n \sim 80-100$.

While the general physical picture is well accepted, and the regime of the transition from van der Walls to covalent nature is well bracketed, there is no clear knowledge concerning the size dependence of the band closure in mercury clusters. The subject matter of this paper is to provide this lacking information. We report here on the photoelectron spectroscopy (PES) of mass-selected negatively charged mercury clusters. We maintain that the observed gap in the PES of these clusters is practically the s-p excitation energy of the corresponding neutral clusters. The basic assumption made here is that the equilibrium geometry of the negatively charged and the corresponding neutral clusters is essentially identical. This assumption is most likely to be valid for the larger clusters in this study.

Our argument is that the excess electron in the negatively charged cluster Hg^-_n resides in the lowest unoccupied molecular orbital (LUMO) of the corresponding neutral cluster. Upon photoexcitation the LUMO electron can be detached, leaving the resulting neutral cluster in its ground state. Alternatively, electrons are detached from the $2n$ states of the $6s$ band of the mercury cluster, leaving the resulting neutral in an "electron-hole pair" excited state. The lowest binding energy in the congestion of the $6s$ electrons belongs to the highest occupied molecular orbital (HOMO). It is thus the HOMO-LUMO gap in the PES of the negatively charged cluster which provides the excitation band gap for the corresponding neutral cluster [10]. We show that these studies provide a much higher cluster size value for the s-p band merging in mercury clusters than previously anticipated values.

Clusters were generated by passing 2.5 bars of argon through an internal heated reservoir of mercury (200–250 °C) of a 15 Hz pulsed nozzle [11]. The expansion was intersected by a pulsed electron beam (~200 eV) generating a wide distribution of negatively and positively charged mercury clusters. The beam was skimmed into a second vacuum chamber, and Hg^-_n clusters were mass resolved with a 1400 eV reflecting time-of-flight mass spectrometer (RTOFMS) [12], perpendicular to the beam axis. To allow for high mass operation of the RTOFMS (up to the 50 000 dalton), we have modified the reflector to include adjustable tilting in order to compensate for the transversal thermal kinetic energy of the clusters. Photoelectron spectra of the mass-resolved clusters were taken with 0.5 mJ fluorine laser (7.9 eV) using a "magnetic-bottle" time of flight PES spectrometer [13]. Because of the high mass of the clusters and their low

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velocity, Doppler broadening did not affect the PES resolution. Therefore, it was unnecessary to decelerate the clusters prior to the photodetachment [13]. Spectra were accumulated, typically with 25 000 double shots (with and without clusters at the detachment zone) for background subtraction. Typical signal and background per laser shot were 1–10 and 5 photoelectrons, respectively. The spectrometer was calibrated daily with the PES of I^- ions [14] with 4.66 and 7.9 eV photons.

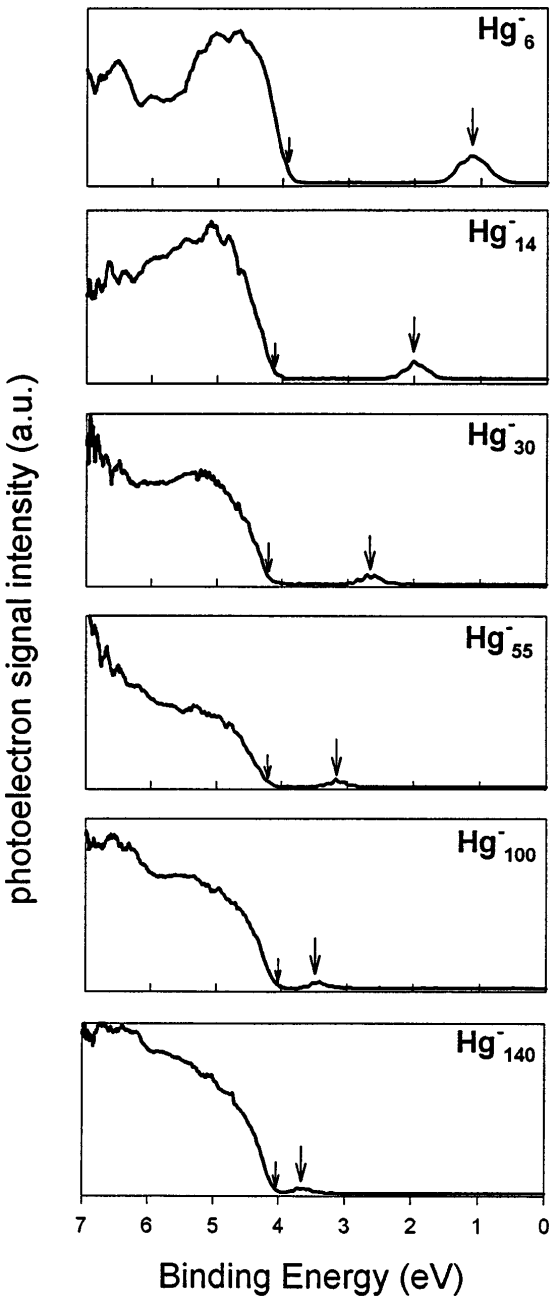

FIG. 1. Selected photoelectron spectra of negatively charged Hg^-_n clusters taken with 7.9 eV laser excitation. The arrows mark the evaluated energies of the HOMO and LUMO binding energies.

PES of Hg^-_n were recorded in the size range of $n = 3-250$. The smallest negatively charged mercury cluster discernible in the mass spectrum was Hg^-_3. In the size range of 3–70 individual mass peaks were well resolved in the mass spectrum. At larger cluster size, peaks were progressively merged, due to the isotope distribution of

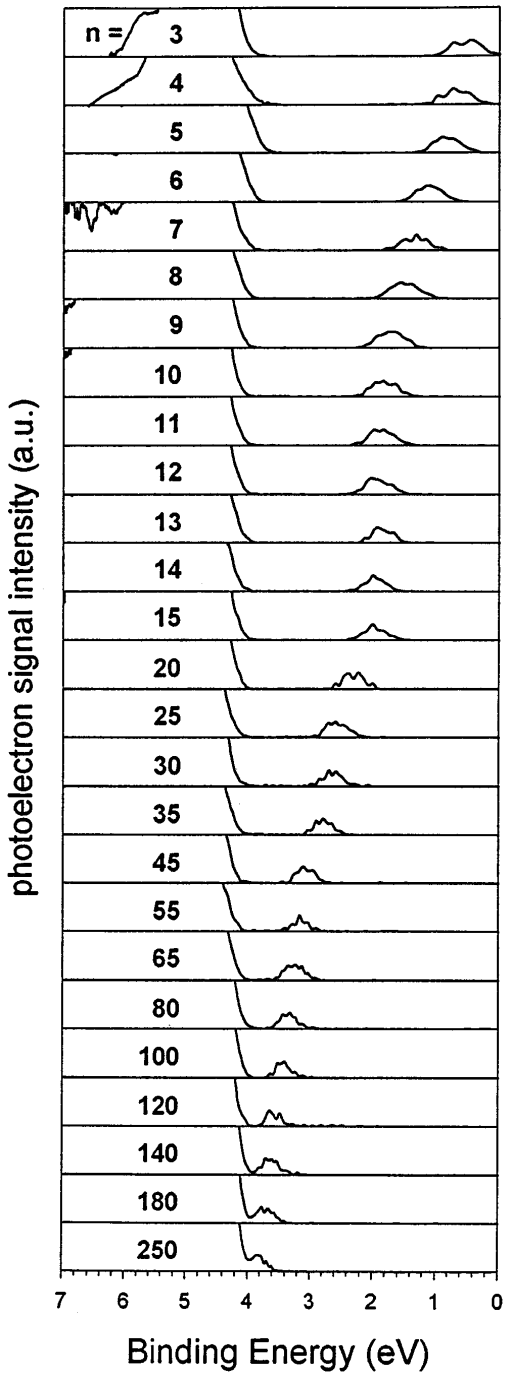

FIG. 2. Photoelectron spectra of Hg^-_n in the size range of $n = 3-250$ taken with 7.9 eV laser excitation. The spectra are scaled and truncated to show a constant intensity of the single peak of the detached $6p$ electron. The fine structure of the $6p$ peaks is due to statistical scatter of photoelectron counts.

mercury as well as to dissociation during the flight time. Consequently, the PES of $n > 70$ represent size uncertainty of ± 1. In Fig. 1 we present 5 representative PES of Hg^-_n. These spectra reveal the following characteristics: A gap is discernible in all the spectra, shrinking monotonically with the increasing cluster size. The ratio between the isolated peak and the band structure in the band shrinks with the cluster size. This last phenomenon is consistent with our interpretation of the PES spectra. The isolated peak is assigned to the detachment of the single excess $6p$ electron occupying the LUMO of the corresponding neutral cluster, while the wide band structure in the PES results from the detachment of the $2n$ electrons residing in the $6s$ valence band. Therefore, under the assumption of similar detachment cross sections for the s and the p electrons the relative weight of the p peak should shrink as n^{-1}.

All of our PES data are presented in Fig. 2. They are normalized and sectioned to present a constant intensity of the single $6p$ peak. This presentation emphasizes the gradual shrinking of the band gap with increasing cluster size.

In Fig. 3 and Table I we summarize the binding energies (BE) extracted from our PES spectra. They include the electron affinities (EA), the BE of the HOMO of the $6s$ band (namely, the smallest BE of the $6s$ band) and the band gap for the s-p excitation (namely, the energy difference of these two values). The BE of the LUMO were evaluated as the center of the isolated peaks in the PES, while those of the HOMO by extrapolating from the steep slope of the $6s$ bands. The arrows in the PES of Fig. 1 mark the evaluated BEs.

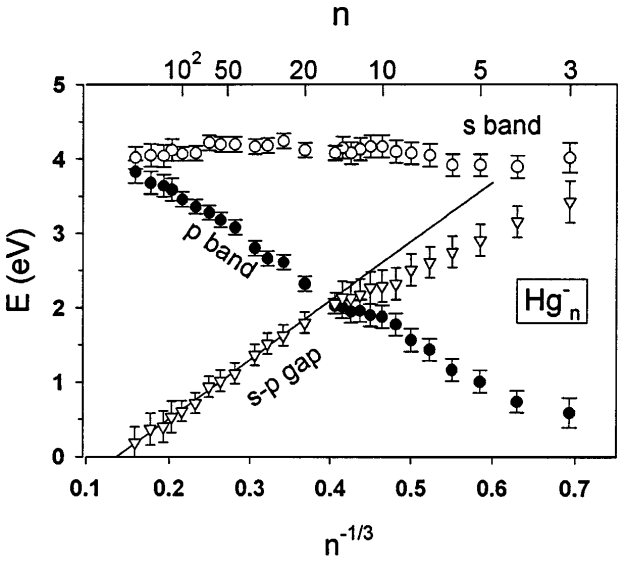

FIG. 3. The size dependence of the BEs of the $6s$ HOMO (open circles) and the $6p$ (full circles) electrons in the PES of Hg^-_n. The s-p band gap is the difference between these values (open triangles). The linear fitting of the band gap, in the size range $n = 50-250$, extrapolates to zero at $n = 400 \pm 30$.

We note in passing that the EA extracted from our PES spectra are by 0.4–0.8 eV higher than the EA of the recent *ab initio* calculations by Dolg and Flad [15]. It seems that their geometry optimized calculations overestimate the internuclear distances. By applying the bulk densities to Hg^-_{13} and to Hg^-_{15} their EA practically coincide with our results (within the 0.1 eV experimental uncertainty).

The following trends in the PES of Hg^-_n should be emphasized: The EA of the clusters increase monotonically with increasing cluster size, reflecting the combination of two complementing trends. The decreasing charging effects of the excess electron, and the widening of the $6p$ band in the neutral cluster, combine to stabilize the excess electron occupying the LUMO of the corresponding neutral cluster. The BE of HOMO hardly changes with cluster size. The HOMO energy in the neutral cluster increases with increasing cluster size, due to band widening, while the charging energy of the cluster decreases. The compensation of these two opposing effects results in a practically constant BE.

TABLE I. The binding energies (BE) of $6p$ excess electron and the HOMO electrons of the $6s$ in negatively charged mercury clusters Hg^-_n in the size range of $n = 3-250$.

Hg^-_n	Be—p band[a] (eV)	Be—s band[a] (eV)	Band gap[b] (eV)
3	0.59	4.02	3.43
4	0.74	3.9	3.16
5	1.01	3.92	2.91
6	1.17	3.92	2.75
7	1.44	4.05	2.61
8	1.57	4.08	2.51
9	1.78	4.1	2.32
10	1.88	4.17	2.29
11	1.9	4.17	2.27
12	1.96	4.13	2.17
13	1.95	4.08	2.13
14	2.01	4.15	2.14
15	2.02	4.08	2.06
20	2.32	4.12	1.8
25	2.61	4.24	1.63
30	2.66	4.18	1.52
35	2.8	4.17	1.37
45	3.08	4.2	1.12
55	3.18	4.2	1.02
65	3.28	4.22	0.94
80	3.36	4.08	0.72
100	3.46	4.07	0.61
120	3.59	4.12	0.53
140	3.64	4.04	0.4
180	3.68	4.05	0.37
250	3.83	4.02	0.19

[a]Estimated error $\Delta(n)$ in eV are 0.2(3); 0.15(4–14); 0.10(15–100); 0.15(120–250).
[b]Estimated error is $2^{1/2}\Delta$.

Our main interest lies in the regular shrinking of the band gap. The inspection of the PES of Hg^-_{250} reveals that, even at this size, the $6p$ peak does not merge into the $6s$ band. The band gap values versus $n^{-1/3}$ were linearly fitted for the cluster size range of $n = 55-250$, as shown in Fig. 3. Note that the well fitted line of the s-p band gap deviates substantially from the experimental data for $n < 15 \pm 2$. This deviation may indicate a different nature in the electronic structure of small neutral mercury clusters. This deviation coincides with the van der Waals to covalent-binding transition identified in several previous experimental and theoretical studies [3–5,7] at the same size range.

Extrapolation of the fitted function to higher cluster size indicates complete band-gap closure at the size range of $n = 400 \pm 30$. This evaluation is based on the direct measurement of the s-p band gap, and is considerably higher than previously reported estimates ($n = 80-100$). Our results indicate that previous experimental criteria for the band closure are not appropriate, and call for a refined theoretical formulation of the electronic structure of mercury clusters.

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Note added in proof.—Unpublished results from Langosch [16] show that the ionization potentials of neutral mercury clusters Hg_n are higher than the classical extrapolation up to $n = 540$ (approximately 0.5 eV) [17].

[1] *Clusters of Atoms and Molecules I*, edited by H. Haberland (Springer-Verlag, Berlin, 1995).
[2] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[3] G. M. Pastor and K. H. Bennemann, in Ref. [1], pp. 86–113; G. M. Pastor, P. Stampfli, and K. H. Bennemann, Z. Phys. D **12**, 365 (1989).
[4] C. Brechignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labasie, and L. Wöste, Chem. Phys. Lett. **120**, 559 (1985); C. Brechignac, M. Broyer, P. Cahuzac, G. Delacretaz, P. Labasie, J. P. Wolf, and L. Wöste, Phys. Rev. Lett. **60**, 275 (1988).
[5] H. Haberland, B. von Issendorff, Y. Yufeng, and T. Kolar, Phys. Rev. Lett. **69**, 3212 (1992); K. Rademann, O. Dimopoulou-Rademann, M. Schlauf, U. Even, and F. Hensel, Phys. Rev. Lett. **69**, 3208 (1992).
[6] H. Haberland, H. Kornmeier, H. Langosch, M. Oschwald, and G. Tanner, J. Chem. Soc. Faraday Trans. **86**, 2473–2481 (1990).
[7] B. Kaiser and K. Rademann, Phys. Rev. Lett. **69**, 3204 (1992).
[8] K. Rademann, B. Kaiser, U. Even, and F. Hensel, Phys. Rev. Lett. **59**, 2319 (1987); K. Rademann, Ber. Bunsen-Ges. Phys. Chem. **93**, 653 (1989).
[9] That is, G. M. Pastor, P. Stampfli, and K. H. Bennemann, Europhys. Lett. **7**, 419 (1988); G. M. Pastor, P. Stampfli, and K. H. Bennemann, Z. Phys. D **12**, 365 (1989); M. E. Garcia, G. M. Pastor, and K. H. Bennemann, Phys. Rev. Lett. **67**, 1142 (1991).
[10] The idea of using the PES of negatively charged clusters to determine the band gap in semiconductor clusters has been suggested already in the first PES studies in clusters. O. Chesnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, and R. E. Smalley, Chem. Phys. Lett. **138**, 119 (1987). This idea was of limited usefulness to the systematic study of band gaps in semiconductor clusters due to the very strong dependence of structure and of dangling bonds on the size and the charge state of the cluster. See also Y. Negishi, H. Kawamata, T. Hayase, M. Gomei, R. Kishi, F. Hayakawa, A. Nakajima, and K. Kaya, Chem. Phys. Lett. **269**, 199 (1997).
[11] D. Bahat, O. Chesnovsky, U. Even, N. Lavie, and Y. Magen, J. Phys. Chem. **91**, 2460 (1987).
[12] G. Markovich, S. Pollack, R. Giniger, and O. Chesnovsky, J. Chem. Phys. **101**, 9344 (1994).
[13] P. Kruit and F. H. Read, J. Phys. E **16**, 313 (1983); O. Chesnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, and R. E. Smalley, Rev. Sci. Instrum. **58**, 2131 (1987).
[14] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[15] M. Dolg and H-J. Flad, Mol. Phys. **91**, 815 (1997).
[16] H. Langosch, Ph.D. thesis, Universitat Freiburg, Germany.
[17] H. Haberland (private communication).