Size Dependence of the Gradual Transition to Metallic Properties in Isolated Mercury Clusters

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Single-photon ionization thresholds are reported for mercury clusters with up to 70 atoms prepared in a supersonic beam. The size dependence of the ionization potentials provides the first direct experimental evidence that a heretofore undetected size-dependent gradual transition from van der Waals–type to metallic properties occurs for mercury clusters in the size range between 20 and approximately 70 atoms.

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The study of the properties of metal clusters has attracted considerable experimental as well as theoretical attention during the last ten years. It is the subject of various review articles and conference proceedings devoted to selected topics.[1] Much of the work has been motivated by a strong interest in the development of metallic properties, as a function of the degree of aggregation, with applications to processes in surface science, heterogeneous catalysis, and microelectronics. In spite of this high level of interest, and in spite of the remarkable progress made, it is still true that the nature of the size-dependent changes in electronic structure of metal clusters is not yet well understood. In particular, there still remains a fundamental controversy about the electronic structure of group-IIA and -IIB metals for which a size-dependent metal-nonmetal transition has been postulated.[2–5] Experiments on the ionization potentials[6,7] of clusters of Hg_x up to $x=12$ and on inner-shell photoionization spectra[8,9] of Hg_x clusters up to $x=8$ indicate that small aggregates of these metals appear to be van der Waals clusters. The photoionization spectra exhibit two strong autoionization features which can be rationalized in terms of transitions from narrow $5d$-derived bands to the center of a $6p$-derived empty band. The doublet remains spectrally well defined up to Hg_8 and a comparison with solid-state experimental data[10] shows that there is no indication of a mixing of the fully occupied $6s$-derived valence band and the empty $6p$-derived conduction band throughout this size range.

In this Letter we report experimental results which we regard as compelling evidence that a size-dependent gradual transition from van der Waals–type to metallic interaction occurs in the Hg_x clusters for $x>20$. As far as we know this transition has never before been observed in the literature.

We used the photoionization technique coupled with time-of-flight spectrometry to determine the ionization potentials which appear to be particularly suitable for investigation of the development of metallic properties with increasing mercury particle size. Details of the experimental apparatus employed in the present measurements are given elsewhere.[11] Basically, it utilizes a normal molecular-beam apparatus consisting of three differentially pumped chambers to produce an intense doubly skimmed seeded or nonseeded supersonic molecular beam of neutral metal clusters. The species to be investigated are generated as follows: Mercury metal is vaporized in a high-temperature stainless-steel oven and the resulting vapor species are coexpanded with a rare gas (Ar or Xe) through a 400-μm-diam conical or 300-μm-diam cylindrical nozzle into a vacuum chamber. Once formed, the clusters enter through two skimmers into the detection chamber which is maintained at a background pressure of about 10^{-6} mbar under typical operating conditions. Single-photon ionization of the clusters in the beam is accomplished by use of an intense and very fast monochromatic light pulse which is focused onto the molecular beam (each pulse lasting about 1 nsec at repetition rates adjustable between 0.5 and 500 kHz). The light pulse is provided by a home-built very fast-discharge light source in high-pressure nitrogen or hydrogen gas (about 1 bar) similar in design and performance to the one described by Bahat *et al.*[12] Its spectral output, containing some sharp lines with high intensities at 10.6, 10.4, 8.3, 7.1, 6.5, and 5.9 eV for N_2 and at 7.7 eV for H_2, extends from the vacuum uv (i.e., from the cutoff limit of the LiF window at about 11.8 eV) to the visible spectral range. The desired photon energy is selected with a vacuum-uv monochromator. Once the ions are formed by the flashlight pulse, they are mass analyzed in a modified[12] Wiley-McLaren time-of-flight mass spectrometer[13] with a resolution $(m/\Delta m)$ of 100, detected with a Daley-type detector,[14] and pulse counted. The counts are time correlated, collected in a time-to-digital converter, and stored in a multichannel analyzer.

Figure 1 shows a selection of typical photoionization mass spectra of mercury clusters obtained with seeded [Fig. 1(a)] and nonseeded [Figs. 1(b) and 1(c)] supersonic beam expansions. The figure caption summarizes the expansion conditions. In the present experiment we observe that cluster distributions are mainly dependent on expansion conditions. Any desired mass spectrum in the size range between Hg and Hg_{100} can easily be obtained by a change in the appropriate expansion parameter such as, Hg pressure in the oven, seed gas to Hg pres-

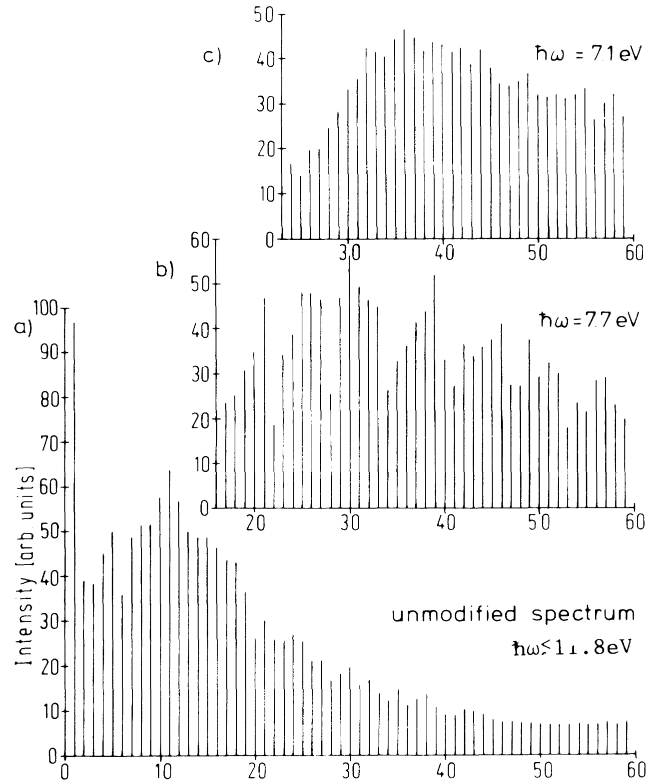

FIG. 1. Selected data showing the results of photoionization mass spectra for three different expansion conditions and different photon energies of the ionizing light. The mass spectra upon which these representations are based are obtained at a resolution $(m/\Delta m)$ of 100. (a) Xe-seeded beam with a tubular nozzle; (b),(c) nonseeded beams with conically shaped nozzles.

sure ratio, temperature, and shape of the nozzle. In particular, we find that the conically shaped nozzle influences the expansion in such a way as to produce distributions of clusters with ion abundance maxima at large cluster sizes [see, e.g., Figs. 1(b) and 1(c)].

TABLE I. Ionization potentials I_p of Hg_x clusters. Work function of the metal: 4.5 eV.

	I_p (eV)	
x	a	b
1	10.43	10.4
2	9.40	...
3	8.90	...
4	8.65	...
5	8.60	...
6	8.50	...
7	8.35	...
8	8.28	8.3
9	8.25	...
10	8.25	...
11	8.22	...
12	8.12	...
17	...	7.7
24	...	7.1
35	...	6.5
49	...	6.2
70	...	5.9

[a] Data taken from Ref. 7.

[b] This work.

In order to relate the mass-spectral ion intensities to the size distribution of the neutral precursor clusters, we assume that the main mechanism for ion formation is single-photon ionization of the neutral clusters without concomitant fragmentation. In this case the observed cluster-ion intensities are a convolution of the abundance and ionization cross sections of the precursor neutral clusters, the mass spectrometer acceptance, transmission, and detection functions, and the intensity of the monochromatic light pulse. We base this assumption on the following noteworthy observation: Variation of the photon energy of the monochromatic photoionizing light pulse for otherwise unchanged expansion conditions only shifts the low-mass threshold of the mass spectrum, while the heights and the positions of the ion abundance maxima are nearly unaltered. This immediately shows that ionization-induced fragmentation is an unimportant process in the present experiment, and that the heavier clusters have the lower ionization potentials. The ionization potentials of mercury clusters for $x < 13$ (Ref. 7) were shown to decrease smoothly and we assume this smooth trend to continue for larger clusters. With ionizing photons of energies $\hbar\omega = 8.3$, 7.7, 7.1, 6.5, 6.2, and 5.9 eV only clusters larger than Hg_8, Hg_{17} [Fig. 1(b)], Hg_{24} [Fig. 1(c)], Hg_{35}, Hg_{49}, and Hg_{70}, respectively, are observable in the mass spectra, whereas with the unmodified broad-band light of the flash ($11.8 \gtrsim \hbar\omega \gtrsim 5$ eV) [Fig. 1(a)] all particles between Hg and Hg_{60} appear in the mass spectrum. A given discrete photon energy is set equal to the ionization potential of the lowest mass observed. The ionization thresholds for Hg_x obtained in this way are listed in Table I together with the results determined by Cabaud, Hoareua, and Melinon[7] in the size range $1 \leq x \leq 12$. A direct comparison of the results for Hg and Hg_8 gives excellent agreement.

It is instructive to compare the experimental values of the ionization potentials with the classical electrostatic equation which gives the energy necessary to remove an electron from a uniformly conducting sphere having the same dimension as the cluster. The appropriate expression[15,16] which connects cluster ionization potentials with the bulk polycrystalline work function by a $1/R$ term, with clusters having higher ionization potentials for smaller particle size, is

$$I_p = w + \tfrac{1}{2}(e^2/R), \tag{1}$$

where w represents the work function, R the radius of the equivalent sphere, and e the elementary charge. A spherical geometry is chosen for comparison and the re-

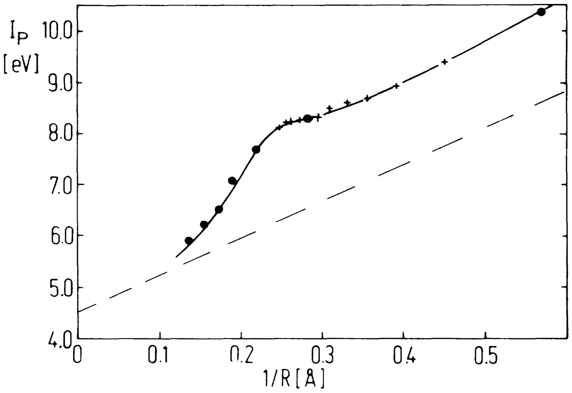

FIG. 2. Comparison of the experimentally determined ionization potential data with the predictions of the classical spherical-droplet model [dashed line, Eq. (1); circles, this work; crosses, data taken from Ref. 7]. We plot the ionization potential vs $1/R$, with R the radius of a sphere with the same volume as an x-atomic metal cluster (assuming atomic volume derived from bulk metallic density).

sults are shown in Fig. 2. We use the most recent results for the work function, $w = 4.49$ eV, of Cotti *et al.*[17] The size of the mercury atom in the bulk metal is chosen to relate the radius R of an equivalent sphere to the number x of atoms in the cluster, so that R varies as the $\frac{1}{3}$ power of x. It is evident that the classical expression, which is found to be in fair agreement with experimental data for large alkali-metal clusters,[15,16] is not in accord with the experimental findings for mercury. There is a significant discrepancy of about 2 eV between predicted and experimentally determined ionization potentials of Hg_x clusters for $x \lesssim 20$. However, the most interesting feature of the data is the relatively rapid decrease of the ionization potentials with increasing cluster size, i.e., increasing R, for $x \gtrsim 20$. The deviation between the measured data and the classical spherical droplet prediction decreases continuously. We regard the fact that the I_p of Hg_{70} is approaching the classical straight line in Fig. 2 as an indication that clusters composed of about 70 and more atoms should exhibit an electronic level structure similar to the metallic bulk material.

In conclusion we find that for small aggregates composed of mercury atoms it makes sense to distinguish between two extreme situations, i.e., the metallic and the van der Waals–type modifications. Mercury atoms, which have a s^2 atomic configuration that is widely separated in energy from the first unoccupied atomic p orbital, give rise to small clusters with fully occupied, van der Waals–type, weakly bonding, s bands. The transformation to the observed bulklike metallic cohesion for large Hg_x clusters ($x > 70$) can only be achieved via overlap of the full s-derived valence band and the empty p-derived conduction band. The experimental results indicate that for Hg_x clusters the evolution of the electronic properties of the bulk metal occurs gradually with increasing particle size in the size range $20 \lesssim x \lesssim 70$.[18]

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[1] See, e.g., *Proceedings of the International Symposium on the Physics and Chemistry of Small Clusters,* edited by P. Jena (Wiley, New York, 1987); see also the special issues of the following journals: J. Phys. Chem. **91**, No. 10 (1987); Ber. Bunsenges. Phys. Chem. **88**, No. 3 (1984); Surf. Sci. **106**, Nos. 1–3 (1981), and **165** (1985); Z. Phys. D 3, Nos. 2 and 3 (1986).

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[18] The situation is somewhat more complicated, as there is also the possibility that a mercury cluster has a metallic core, surrounded by a nonmetallic surface layer. The existence of such a partial monolayer of nonmetallic atoms adsorbed on the metal surface has been suggested by M. F. D'Evelyn and S. A. Rice, J. Chem. Phys. **78**, 5082 (1983), to account for experimental results on the optical constants [A. M. Bloch and S. A. Rice, Phys. Rev. **185**, 933 (1969)] and x-ray reflection data of liquid mercury [B. C. Lu and S. A. Rice, J. Chem. Phys. **68**, 5558 (1978)]. They found that the metal-nonmetal transition which occurs across the interface plays a critical role in determining the liquid-vapor interface structure.