Probing the Transition from van der Waals to Metallic Mercury Clusters

C. Bréchignac,[a] M. Broyer,[b] Ph. Cahuzac,[a] G. Delacretaz,[c] P. Labastie,[b] J. P. Wolf,[c]
and L. Wöste[c]

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud,
91405 Orsay Cedex, France

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Inner-shell autoionization spectra obtained with synchrotron radiation are reported for mercury clusters Hg_n, $n \leq 40$. For the small clusters $n \leq 12$ the spectral behavior as a function of size is interpreted in terms of an excitonic model. For larger cluster sizes a gradual deviation from van der Waals bonding is observed. The asymmetry occurring in the line profiles reflects the progressive construction of the *sp* conduction band.

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It is of fundamental interest to know how the occupied atomic states that contain the valence electrons of metal atoms are broadened to form the band structure of a solid. Particularly interesting in this respect are the divalent metals[1] which, as free atoms, have an s^2 closed-shell atomic configuration, and should in principle be insulators in the bulk. It is well known that the metallic character of the divalent metals is due to the overlap between the filled *s* and the empty *p* bands. To probe the evolution from the van der Waals to metallic bonding in divalent metal systems one can proceed in two different ways.

From a *macroscopic* point of view, starting from an atomic vapor and reducing the interatomic separation will lead to a situation of overlapping *s* and *p* electron states. This should correspond to an insulator-metal transition. In the case of mercury, experiments on electrical conductivity,[2] Hall effect,[3] Knight shift,[4] and optical-absorption coefficient measurements[5] indicate that at densities of mercury between 5.5 and 8 g/cm^3 the *s*-like states are separated from the unoccupied *p*-like band states, whereas this gap vanishes at higher densities. These experiments illustrate the metal-nonmetal transition in a macroscopic system.

On the other hand, from a *microscopic* point of view, new insight into the construction of metallic bands can be obtained by the variation of the nearest-neighbor coordination. This can be achieved by our following the evolution of electronic properties of metal clusters as their size gradually increases. Up to now most of the experiments which have been done deal with ionization-potential measurements. In the case of mercury, ionization potentials were first measured by Hermann[6] and Cabaud, Hoareau, and Melinon[7] by electron-impact ionization, and further measurements have been recently extended to higher masses.[8,9] Such measurements provide the energy difference between the electronic ground states of the neutral and the cluster ion. Since the size evolution of each electronic structure (neutral and ion) may be different, the interpretation of ionization-potential behavior as a function of cluster size is not straightforward. For the very large mercury clusters Hg_n, $n \geq 10^3$, following Kubo's criterion[10] the density of states near the Fermi level is large enough to produce metallic structure for both the neutral particle and its ion. In contrast, for small cluster sizes the molecular point of view prevails and the electronic structures of the neutral and the ionized cluster are radically different. This is illustrated in the mercury dimer for which the binding energy of the neutral dimer Hg_2 is 0.07 ± 0.02 eV,[11] whereas the binding energy of the ion $Hg_2{}^+$ is 1.40 ± 0.02 eV.[12]

An alternative way to probe the electronic structure of the small mercury clusters is to follow the spectral evolution of inner-shell–valence transitions for which a core electron is excited to a valence level.[13] Since the core electrons remain practically localized from the atom to the bulk,[14] such transitions mostly probe the behavior of the valence level as a function of cluster size. In this Letter we report on the size dependence of the $5d$ - $6p$ core-valence autoionization mercury lines up to Hg_{40}. The results concerning their broadening and their shift provide new insight into the electronic states of mercury.

The molecular-cluster-beam apparatus has been described elsewhere.[15] The basic elements of the setup are as follows. The mercury clusters are formed in an adiabatic expansion of a pure mercury vapor through a 0.3-mm-diam conical nozzle in order to obtain large cluster sizes. The stagnation pressure is of the order of 1 atm. The clusters are mass selected by a commercial quadrupole mass spectrometer, modified to reach more than 8000 mass units.[16] The mass quadrupole is axially oriented to the cluster beam. A typical mass spectrum is shown in Fig. 1. The differentially pumped quadrupole chamber is connected to a monochromatized undulator radiation exit of the Anneaux de Collisions de l'Accélérateur Linéaire d'Orsay storage ring. The light coming from the undulator, providing more than 10^{12} photons Å^{-1} s^{-1}, is focused at right angles to the neutral beam and photoionizes the clusters. The photoionization

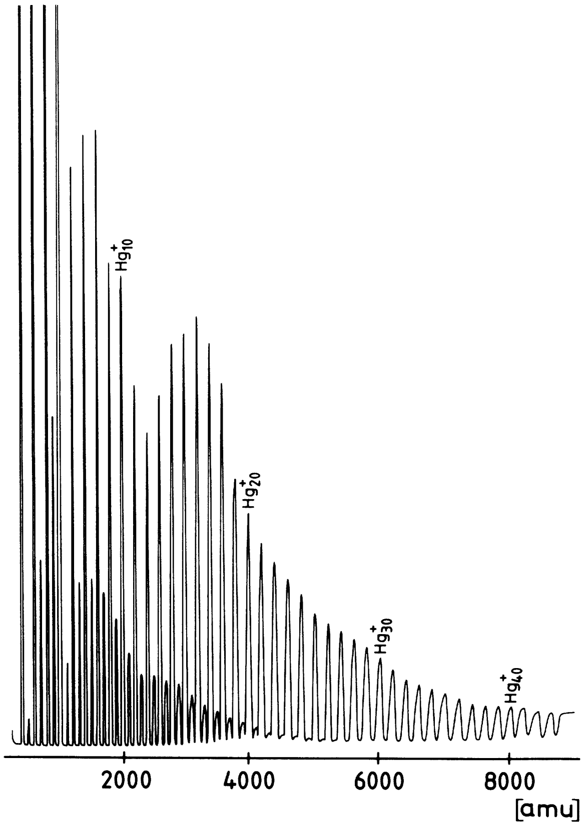


FIG. 1. Typical mass spectrum of mercury cluster beam obtained by electron-impact ionization at electron energy of 60 eV. The congruent behavior of singly and doubly charged clusters indicates that the fragmentation processes are not very significant.

efficiency (PIE) curve of each mass-selected cluster ion is monitored by the variation of the photon energy.

The PIE curve of the atom is recorded between the ionization thresholds $\mathrm{Hg}(5d^{10}6s^2) \rightarrow \mathrm{Hg}^+(5d^{10}6s)$ and $\mathrm{Hg}(5d^{10}6s^2) \rightarrow \mathrm{Hg}^+(5d^96s^2)$ corresponding to the ejection of one *s* electron or one *d* electron, respectively. In this energy region (10–16 eV) the observed autoionization structures assigned to Rydberg transitions are similar to observations by Linn *et al.*[12] We consider in more detail the transitions

$$\mathrm{Hg}(5d^{10}6s^2\,{}^1S_0) \rightarrow \mathrm{Hg}^*[5d^96s^2(D_{5/2,3/2})6p] \tag{1}$$

in which a 5*d* core electron is excited into the 6*p* lowest unoccupied valence state. If the energy of this transition is larger than the ionization potential, such excitation gives rise to electron-exchange ionization which takes place on a 10^{-13}-s time scale[17]:

$$\mathrm{Hg}^*(5d^96s^26p) \rightarrow \mathrm{Hg}^+(5d^{10}6s) + e^-.$$

For the atom only the $D_{3/2}$ state leads to autoionization process whereas for Hg_n, $n \geq 2$, both the $D_{3/2}$ and $D_{5/2}$ states induce autoionization. The corresponding ion intensities depend on the absorption probability and on autoionization cross section. For the atom and the dimer the line intensities are 3 orders of magnitude larger than the direct ionization,[12,13] whereas for clusters and the bulk nothing is known of the autoionization probability.

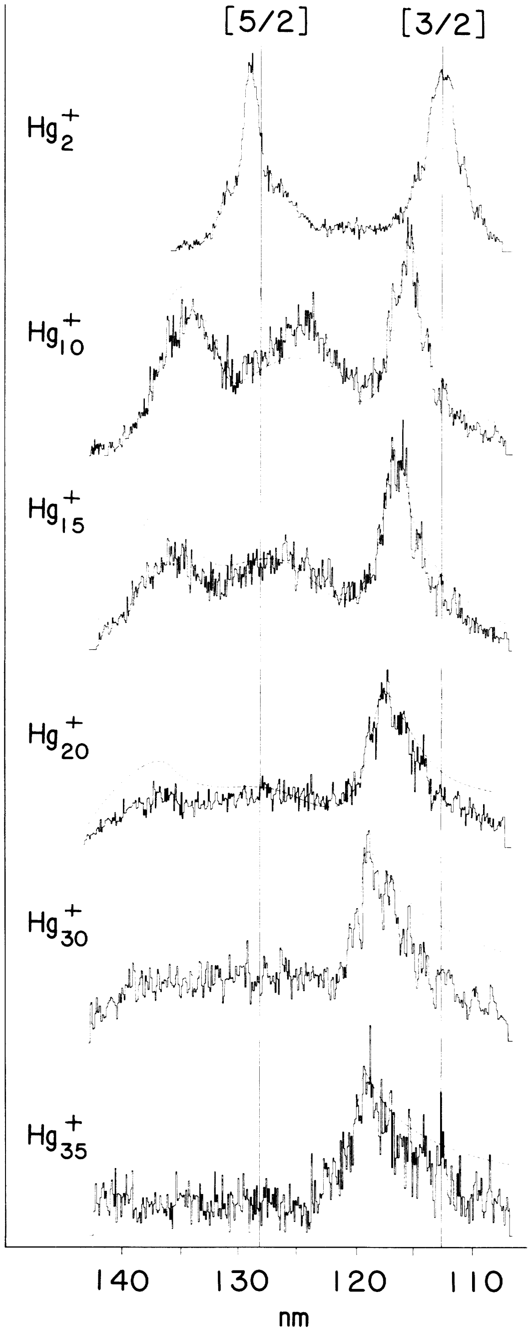
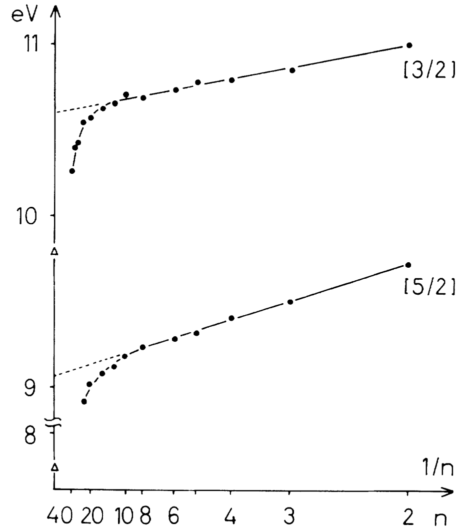


FIG. 2. Solid lines: the recorded PIE curves obtained for some mercury clusters in the energy range 8.5 to 11.5 eV. A cutoff LF filter is used to suppress overtones. Dashed lines: the normalized intensity; vertical straight lines represent atomic positions.

Since the autoionization takes place in 10^{-13} s the fragmentation effects should not exist in the neutral cluster between its excitation and its ionization. However, after the autoionization the excess of energy is either taken by the emerging electron or redistributed in the ion. In the latter case fragmentation could occur during the flight time after ionization and before the detection and should be taken into account. For the small cluster masses the fragmentation effect has not been observed. For the large masses, if it exists, this leads to an uncertainty of one mass unit at most. The PIE curves of clusters recorded in the energy range 8.5 to 11.5 eV are shown in Fig. 2. Besides the two main autoionization lines $D_{5/2}$ and $D_{3/2}$ an unassigned component appears. It may be due to a forbidden transition in both the monomer and the dimer, which would become allowed in the cluster by molecular interactions.

For small clusters Hg_n with $n \leq 12$ the two autoionization lines are well resolved and appear red shifted with respect to the corresponding atomic transitions. The peak energies are inversely proportional to the number of atoms constituting the cluster. This functional dependence is analogous to the excitonic behavior in the independent-electron approximation.[18] The excitonic behavior which is characteristic of a van der Waals system[19-21] gives the evidence for the insulating character of small mercury clusters (Fig. 3).

For cluster sizes larger than $n = 13$ the $1/n$ dependence is no longer observed. The measured gradually increasing shift for both lines illustrates the deviation from the van der Waals bonding in larger cluster sizes. It can be understood in terms of a stronger interaction due to correlations between the valence electrons as the cluster becomes more compact, as has been recently calculated.[22] More precisely the deviation from the excitonic behavior which occurs at $n = 13$ may be understood as due to an icosahedron structure of Hg_{13}. In this case a central atom is surrounded by twelve neighbors. Such a compact environment for the central atom tends to increase the interaction between the central atom and the surface atoms, thus enhancing the s-p hybridization.



FIP. 3. Peak energies of the autoionization structure correlated to the $\mathrm{Hg}(5d^{10}6s^2\,{}^1S_0) \rightarrow \mathrm{Hg}^*[5d^9 6s\,{}^2D_{5/2,3/2})6p]$ atomic transitions vs $1/n$. The straight lines illustrate the $1/n$ behavior for the small masses. The triangles for $n = \infty$ are taken from Ref. 17.

In the size range $13 \leq n \leq 20$ the lines broaden significantly as their shifts deviate from the linear behavior. Morever the spin-orbit splitting of the $5d$ levels increases with cluster size, as has been noted elsewhere for the d levels of supported clusters[23] and has been attributed to combined spin-orbit and crystal-field effects.[24] Such an increasing splitting leads to a shift larger for the $\frac{5}{2}$ line than for the $\frac{3}{2}$ line and brings the $\frac{5}{2}$ peak out of the studied energy range.

For larger cluster sizes, $n > 20$, only the $\frac{3}{2}$ peak is considered. In addition to its broadening and shift, its spectral line shape is markedly asymmetric which is qualitatively what we expect to see for a transition from molecular to bulk metal properties. In atomic gas phase the $\mathrm{Hg}(5d^{10}6s^2) \rightarrow \mathrm{Hg}^*(5d^9 6s^2 6p)$ absorption presents a symmetrical line shape.

The corresponding absorption in the bulk, associated with excitation of a $5d$ core electron to the unfilled part of the sp band, leads to a steplike shape towards the high energies (Fig. 4). The degree of asymmetry is thus dependent on the density of states at the Fermi level. The observed $\frac{3}{2}$ autoionization line which presents such an asymmetry from $n = 20$ is the first illustration of a gradual construction of the sp band. However, a rough estimation of the minimum number of atoms needed for metallic behavior based on a large number of states within kT near the Fermi level leads to a few hundred atoms. We deduce that the transition from van der Waals ($n \leq 12$) to metallic mercury clusters takes place

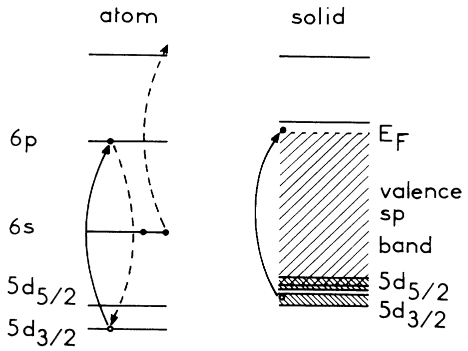


FIG. 4. Binding-energy diagram of monoelectronic levels in mercury. Solid lines represent the absorption for the $5d$ level to the lowest unoccupied $6p$ level. Dashed lines correspond to autoionization process. The deduced spectra from this diagram are discussed in the text.

over a wide cluster size range. From our work we conclude that probing of spectroscopic lines is a sensitive diagnostic of the organization of the electrons in the intermediate region.

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(a)Present address: Laboratoire Aimé Cotton, Bât. 505, 91405 Orsay Cedex, France.

(b)Present address: Laboratoire de Spectrométrie Ionique et Moléculaire, Université Lyon I, Bât. 205, Campus de la Dona, 69622 Villeurbanne Cedex, France.

(c)Also at Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB Ecublens, CH 1015 Lausanne, Switzerland. Present address: Centre d'Application Laser, CH 1015 Lausanne, Switzerland.

[1] A. R. Miedema and J. W. F. Dorleijn, Philos. Mag. B **43**, 251 (1981).

[2] E. V. Franck and F. Henzel, Phys. Rev. **147**, 109 (1966).

[3] U. Even and J. Jortner, Phys. Rev. Lett. **28**, 31 (1972).

[4] U. El-Hanany and W. W. Warren, Jr., Phys. Rev. Lett. **34**, 1276 (1975).

[5] H. Uchtmann and F. Hensel, Phys. Lett. **53**, 239 (1975).

[6] H. Hermann, thesis, Universität Bern, 1978 (unpublished).

[7] B. Cabaud, A. Hoareau, and P. Melinon, J. Phys. D **13**, 1831 (1981).

[8] K. Rademann, B. Kaiser, U. Even, and F. Hensel, Rev. Lett. **59**, 2319 (1987).

[9] H. Kormeier and H. Haberland, to be published.

[10] R. Kubo, A. Kawabata, and S. Kobayashi, Annu. Rev. Mater. Sci. **14**, 49 (1984).

[11] K. Hilpert, J. Chem. Phys. **77**, 1425 (1982).

[12] S. H. Linn, C. L. Liao, C. X. Lia, J. M. Brom, and C. Y. Ng, Chem. Phys. Lett. **105**, 645 (1984).

[13] C. Bréchignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labastie, and L. Wöste, Chem. Phys. Lett. **120**, 559 (1985).

[14] S. Svensson, N. Martensson, E. Basilier, P. Å.Malmqvist, V. Geliusand, and K. Siegbahn, J. Electron Spectrosc. Relat. Phenom. **9**, 51 (1976).

[15] G. Delacretaz, thesis, Ecole Polytechnique Fédérale de Lausanne, 1985 (unpublished).

[16] P. Labastie, to be published.

[17] K. Bartschat and P. Scott, J. Phys. B **18**, L 191 (1985).

[18] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, Eastbourne, Sussex, 1981), p.627.

[19] W. M. Trott, N. C. Blais, and E. A. Walters, J. Chem. Phys. **69**, 3150 (1978).

[20] S. H. Linn, Y. Ono, and C. Y. Ng, J. Chem. Phys. **34**, 3342 (1981).

[21] A. Ding, J. H. Futrell, R. A. Cassidy, L. Cordis, and J. Hesslich, Surf. Sci. **156**, 232 (1985).

[22] G.M. Pastor, P. Stampfli, and K. H. Bennemann, to be published.

[23] G. K. Wertheim. S. B. Dicenzo, and S. E. Youngquist, Phys. Rev. Lett. **51**, 2310 (1983).

[24] M. G. Mason and R. C. Baetzold, J. Chem. Phys. **64**, 271 (1976).