

Photoelectron Spectroscopy of Neutral Mercury Clusters Hg_x ($x \leq 109$) in a Molecular Beam

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(Received 20 February 1992)

Vacuum ultraviolet photoelectron spectra are reported for mercury clusters with up to 109 atoms. These spectra yield quantitative information about the evolution of ionization potentials and bandwidths. Further results about partial photoionization cross sections are obtained by varying the photon energy. The photon energy dependence provides direct experimental evidence that large mercury clusters Hg_x ($x \geq 60$) possess already a high density of p states near E_F .

PACS numbers: 79.60.Cn, 35.20.Vf, 36.40.+d, 71.30.+h

The physical and chemical properties of metal clusters have received a considerable amount of interest during the last decade [1]. This is due to the fact that they possess neither the properties of the single atom nor those of the bulk. They form a completely new class of materials, which often exhibit strong size-dependent effects. One of the basic underlying questions here is, how do the metallic properties of these clusters evolve as a function of size? This is especially true for clusters of group IIA and IIB elements, for which a size-dependent nonmetal to metal transition has been postulated [2,3]. Experimental investigations of the ionization potentials [4-7] and the inner-shell photoionization spectra [8,9] of Hg_x clusters find a size-dependent transition from van der Waals-like to metallic behavior in the size range between 20 and 70 atoms. Several theoretical studies indicate that this transition in clusters of divalent elements is due to a size-dependent sp hybridization, which converges quickly to the bulk value [10-12]. Singh and Dy have applied a first-principles tight-binding linear muffin tin orbital method to investigate the nature of the bonding in Hg_x ($2 \leq x \leq 79$). They found an appreciable increase in p character around $x = 13-19$ (signaling the onset of covalent bonding), and for clusters with $x \geq 79$ the p character approaches the bulk value. More recently, Garcia, Pastor, and Bennemann treated the interplay between van der Waals (intra-atomic sp excitations) and covalent (interatomic sp excitations) interaction explicitly on the same electronic level to study the size dependence of the cohesive energy per atom. Pastor, Stampfli, and Bennemann have calculated the average density of states [s - and p -DOS (DOS denotes density of states)] for Hg_x ($x < 135$), and found that for Hg_{80} the main features of the bulk density of states are already present.

Up to now, however, there has been no detailed experimental information on the size-dependent evolution of the electronic band structure in metal clusters of group IIB and IIA. One of the methods, which is most promising in this respect, is vacuum ultraviolet photoelectron spectroscopy (VUV-PES), because it is as amenable to atoms as to the bulk material, so allowing for a direct comparison to be easily made. Furthermore, it offers access to ionization potentials. By scanning the photon energy, informa-

tion about partial and total photoionization cross sections, and therefore directly about the electronic structure of the system under investigation, is available.

In this Letter we present experimental results regarding the photon energy dependence of the electron distribution curves (EDC's) of large mercury clusters. This can be understood in terms of a varying contribution of the partial photoionization cross sections, which in turn provides compelling evidence that the contribution of p -type electrons to the photoemission spectra of large mercury clusters Hg_x ($x \geq 60$) is already quite large.

We used a newly developed triple-coincidence technique, which is described in detail in Ref. [13]. In short, it comprises a molecular beam apparatus consisting of three differentially pumped chambers to produce an intense supersonic beam of metal clusters. Mercury metal is evaporated from a high-temperature stainless-steel oven through a cylindrical 300- μm -diam or conical 450- μm -diam nozzle with or without a noble gas into vacuum. The clusters, after having been doubly skimmed downstream, enter the detection chamber which has been held at 10^{-5} mbar under operating conditions. Single photon ionization of the clusters is achieved by the monochromatized light of a N_2 -gas discharge lamp, which provides several lines of high intensity in the VUV region. The lamp operates at a high frequency (typically 10-20 kHz). The ionization efficiency is around 5% to 10% to discriminate against double ionization processes. During the light pulse the ionization region is electrostatically field free. The emerging electron is focused by a magnetic bottle-type time-of-flight spectrometer (resolution 150 meV FWHM at 1 eV kinetic energy) to the detector. As soon as the electron is detected, a high voltage pulse is applied to the front plate of the modified Wiley-McLaren-type time-of-flight spectrometer [14] and the corresponding ion is mass analyzed. The time correlated ion and electron counts are collected in two separate time to amplitude converters and the electron signal is stored in a multichannel analyzer. The coincidence count rate is around 3 to 30 counts/sec.

To record the EDC's of liquid mercury, a droplet of mercury is placed with a holder in front of the electron spectrometer and the photoelectron spectra are recorded

directly as a function of the photon energy.

Figure 1 shows EDC's for several selected mercury clusters and for liquid mercury as a function of electron binding energy. These spectra contain the following information: First, one can obtain the ionization potentials from the onset in these curves [15]. The data extracted in this way are in good agreement with data measured by photoionization mass spectroscopy [6] and electron impact ionization [5,7]. Second, one can get information about the evolution of the bandwidth of these clusters. The overlap of $6p$ with $6s$ orbitals forms a 9.25-eV broad conduction band in the bulk, which completely overlaps with the filled $5d_{5/2}$ band [16]. Note the strong increase in bandwidth for clusters with more than 13 atoms. For a cluster containing 109 atoms the bandwidth is already 80% that of the bulk value.

Further information on the electronic structure of these clusters can be obtained from the photon energy dependence of the EDC's. These results are of general interest, because it is expected that the photoionization cross section depends strongly on the photon energy [17], especially near threshold. The integral photoelectron count rate per unit time is given by

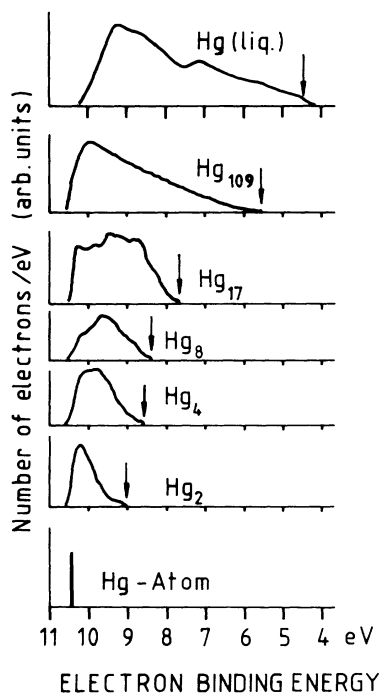


FIG. 1. Photoelectron-photoion-coincidence spectra of mercury clusters with up to 109 atoms recorded at 10.6 eV photon energy. The spectrum of liquid bulk mercury (recorded at 10.2 eV photon energy) has been redrawn from Ref. [25]. The spectra display the photoelectron intensity as a function of the electron binding energy relative to the vacuum level. The vertical arrows indicate the ionization potentials for clusters, and the work function for bulk mercury.

$$\frac{n(e^-)}{t} \propto I_{cl} I(h\nu) \sum_{BE=IP}^{h\nu} I(h\nu, BE) \quad (1)$$

with

$$I(h\nu, BE) = \sum_l \sigma_l(h\nu, BE) n_l(BE),$$

where I_{cl} is the intensity of a selected cluster in the molecular beam, $I(h\nu)$ the intensity of the light source at the photon energy of interest, σ_l the partial photoionization cross sections, n_l the partial density of states, and l the angular momentum. The partial photoionization cross sections are summed over the electron binding energy (BE) range from the ionization potential (IP) to the photon energy ($h\nu$) to yield the absolute photoionization cross section.

Figure 2 shows the EDC's for Hg_{109} at three different photon energies. The integral of the hatched areas (6 to 6.5 eV electron binding energy) is displayed in Fig. 3 as a function of photon energy. There is a strong increase of more than 1 order of magnitude in electron count rate with decreasing photon energy. This increase is neither due to the surface plasmon absorption band of large mercury clusters [18], which is located at 5.95 eV photon energy, nor to autoionization features, whose relative intensities decrease drastically for clusters consisting of more than 30 atoms [9], and which are located at 9.8 eV ($d_{3/2}$) and 7.8 eV ($d_{5/2}$) in the liquid [16]. Furthermore, be-

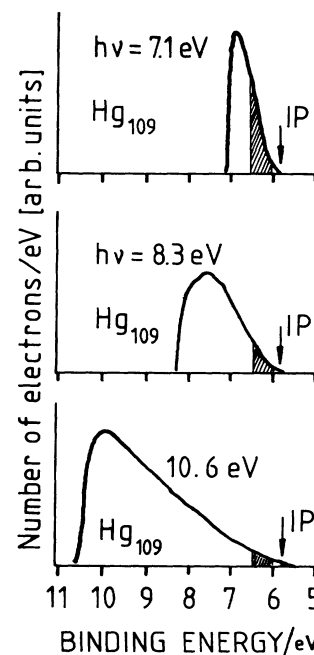


FIG. 2. Photoelectron-photoion-coincidence spectra of cluster Hg_{109} recorded at different photon energies. The hatched areas (between 6 and 6.5 eV binding energy) give the photoemission intensity that is displayed in Fig. 3 as a function of photon energy.

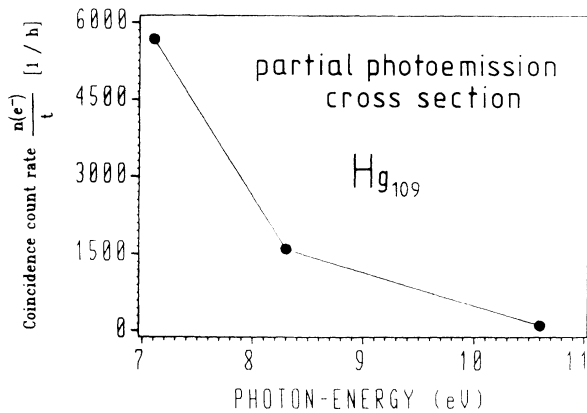


FIG. 3. Photon energy dependence of the electron count rate per unit time for electrons with binding energies between 6 and 6.5 eV for the cluster Hg₁₀₉.

cause during the experiment the intensity of a selected cluster stays nearly constant, the light intensity of our source changes at most by a factor of 3 in this photon energy range [19], and the DOS must be constant, the observed strong increase in electron count rate must be due to a change in the partial photoionization cross sections.

A similarly strong increase in electron count rate is also observed for the EDC's of liquid mercury. Calculations for liquid mercury show that σ_s and σ_p are nearly of equal magnitude for VUV-PES, and that σ_p increases for lower photon energies [17]. Figure 4 displays the normalized count rate in percent for four large mercury clusters and for liquid mercury as a function of photon energy. The normalized rate is obtained by dividing the electron count rate in the electron binding energy region from 6 to 6.5 eV by the integral count rate over the entire binding energy range, thereby eliminating completely cluster and photon intensity dependences, as can be seen from formula 1. This procedure allows us to make a direct comparison between the PES characteristics of liquid mercury and mercury clusters. From Fig. 4 it is obvious that large mercury clusters behave already in the same way as liquid mercury regarding their PES characteristics. Because bulk mercury possesses a high density of p states above and below the Fermi level [12], we conclude that the same is true for large mercury clusters investigated in this experiment. Also theoretical calculations [12] indicate that for x about 80 the main features of the bulk DOS are already present. This trend (evolution of bulklike properties) is further supported by the known ionization potentials, bandwidths, absorption spectra and cohesive energies.

For clusters of other divalent elements (which have not been studied experimentally by now) a rapid evolution of bulklike p character is discussed too. *Ab initio* molecular-dynamics simulations show that for Be clusters the bulk p character is already reached for a cluster consisting of only six atoms [20], and that Mg clusters have al-

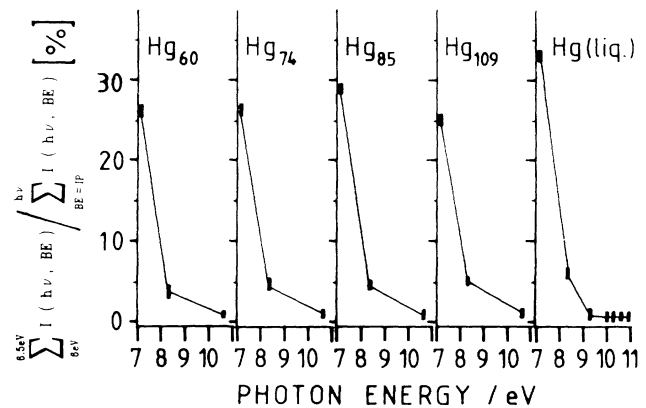


FIG. 4. Comparison of normalized electron count rates (see text) for several large mercury clusters and liquid mercury as a function of photon energy.

ready a considerable amount of p character at Mg₁₃ [21–23]. The difference in p character between the different group-II elements may be understood in terms of the different extension of the atomic orbitals with respect to interatomic distance, and in the different spacing between atomic s and p levels [2,22,24].

In conclusion we have found that large mercury clusters show photon-energy-dependent photoemission characteristics, which can be explained by the different orbital character from which the electrons are ejected. This implies that these clusters have already an appreciable p density of states near the Fermi energy.

We gratefully acknowledge financial support of the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie, and the German-Israeli Foundation (GIF).

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