Transition to Plasmonlike Absorption in Small Hg Clusters

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Optical absorption spectra for mass-selected Hg_n^+ and Hg_n^{++} clusters show an abrupt transition to a collective, plasmonlike absorption as a function of increasing cluster size. The position of the single observed plasmon maximum is independent of the charge state and nearly independent of cluster size. The peak positions agree well with those of the classical Mie plasmon calculated from the experimental dielectric function. The width of the plasmon resonance is discussed and a strong temperature effect is conjectured.

The Hg atom is a fascinating object in cluster physics. Because of its $5d^{10}6s^2$ closed shell electronic structure it is dominantly van der Waals bound for the diatomic molecule and small clusters [1,2]. The widths of the occupied $6s$ band [3] and the empty $6p$ band increase roughly proportional to the number of nearest neighbors. Thus the "band gap" Δ (compare Fig. 1) decreases for increasing cluster size. In the bulk, the $6s$ and $6p$ bands overlap giving bulk Hg its metallic character. The chemical bonding changes from dominantly van der Waals, to covalent, and then to metallic [1, 2]. One thus has a metal-to-nonmetal (MNM) transition as a function of cluster size.

Little is known on the optical properties of Hg clusters. The cluster size dependence of the $5d^{10}6s^2 \rightarrow 5d^9 6s^2 6p$ autoionizing transition has been measured [4]. An absorption spectrum of a neutral, not-mass-selected Hg cluster beam was published [5]. For the bulk, the optical constants of Hg have been measured [6] and calculated [7]. The absorption spectrum of "expanded" mercury has been studied in the context of the MNM transition [8].

The aim of this experiment was to study how the changes in chemical bonding and the MNM transition influence the optical properties of Hg clusters. The apparatus is an improved version of the one used earlier to measure optical spectra for Ar_n^+ and Xe_n^+ clusters [9,
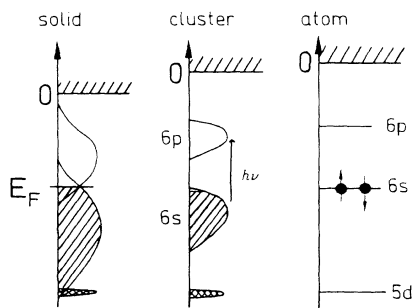

FIG. 1. Electronic configurations of the Hg atom, cluster, and bulk. A metal-to-nonmetal transition occurs as function of the cluster size, when the $6s$ and $6p$ bands start to overlap.

10]. Briefly, an Ar-seeded supersonic expansion generates the clusters. They are ionized by electron impact, and mass separated by a reflectron time-of-flight (TOF) mass spectrometer. Clusters of a single size are irradiated by photons. The electronic excitation is rapidly converted into vibrational energy, leading to ejection of atoms. A second TOF measures the fragment spectrum. Standard "depletion spectroscopy" is used to record the optical spectra [11–17].

The cluster temperature can be estimated from the Klots equation $k_B T \approx D_n^+/24$, where k_B is Boltzmann's constant, and T and D_n^+ are the temperature and dissociation energy of the cluster ion, respectively [18]. The D_n^+ values have been determined experimentally up to $n = 25$ [2]; they agree well with recent calculations [1]. For $n = 10$ one finds $D_{10}^+ \approx 0.2$ eV. For $n = 100$, an educated guess (from Fig. 9 of Ref. [2]) gives $D_{100}^+ \approx 0.58 \pm 0.02$ eV. The estimated cluster temperatures thus increase with cluster size from $T(Hg_{10}^+) \approx 100$ K to $T(Hg_{100}^+) \approx 280$ K.

Figures 2 and 3 show selected data for singly charged and all our data for doubly charged clusters, respectively. These are the first absorption spectra for mass-selected mercury clusters, and—to the best of our knowledge—the first optical data for multiply charged clusters. Sharp lines can be seen for small n, which shift [19] to the red with increasing cluster size. They are probably due to $6s \rightarrow 6p$ transitions, as indicated in Fig. 1. The width of both the $6s$ and $6p$ bands increases, and the band gap Δ decreases, as a function of the cluster size, which makes the observed redshift plausible. A closer inspection shows that there are actually one small and one large maximum, the latter consisting sometimes of two or three peaks. This will be discussed in more detail elsewhere [20]. This fine structure could possibly be the signature of highly correlated electrons [21].

At some small n ($n \geq 6$ for singly charged, and $n \geq 13$ for doubly charged clusters) the intensity of the $6s \rightarrow 6p$ lines decreases rapidly, and a broad unstructured maximum appears at $\hbar\omega \geq 5.0$ eV. As discussed below, this maximum is identified as a collective, "plasmon" type of absorption. The spectrum could be measured only up
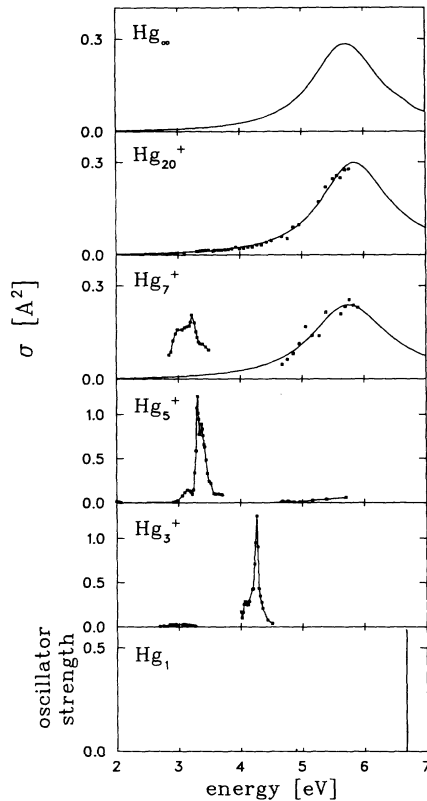
FIG. 2. Experimental photoabsorption of the Hg atom (lowest panel, note the small triplet absorption at 4.9 eV), of $Hg_n{}^+$ clusters, and that calculated for a small, classical sphere of liquid Hg (top panel). The vertical scales are per $6s$ electron. The solid lines for $n = 3$ to 20 are a fit to the data. Note the change of scale between $n = 5$ and 7.

FIG. 3. Experimental photoabsorption spectra of doubly charged Hg clusters.

to 5.9 eV, which is the high-frequency limit of the BBO2 frequency-doubling crystal used. No splitting of the plasmon maximum is observed, in contrast to the alkali-metal case [11–16].

The discussion below will be concerned mainly with the plasmon maximum. The bulk limit, or Mie plasmon, can be obtained easily. The photoabsorption cross section σ_∞ for a classical, small sphere of radius R is given by [22, 23]

$$\sigma_\infty(\omega) = \frac{4\pi\omega}{c}\, R^3\, \mathrm{Im}\left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}\right).\qquad (1)$$

Here Im stands for imaginary part and $\epsilon(\omega)$ is the complex dielectric function. Using the experimental, room-temperature values [6] for $\epsilon(\omega)$ one obtains the spectrum shown in the upper panel of Fig. 2. One broad maximum occurs near $\mathrm{Re}(\epsilon) = -2$, where Re stands for real part. This is the unambiguous sign of a dipolar Mie plasmon [22, 23].

A Drude-like dielectric function [22–24] in Eq. (1) gives

$$\sigma_n(\omega) = \sigma_n(\mathrm{max})\frac{\Gamma^2\omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}.\qquad (2)$$
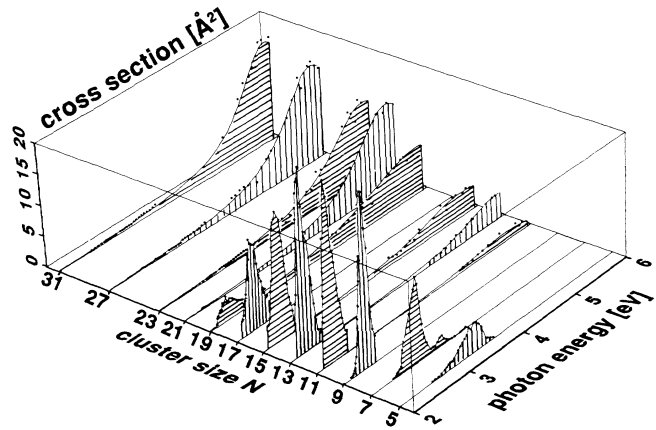
Here $\sigma_n(\mathrm{max})$ is the value of the cross section at the maximum. The resonance frequency ω_0 and the width of the resonance $\hbar\Gamma$ depend on cluster size n. This equation describes reasonably well the plasmon line shapes of the spherical alkali [11–16] and silver [17] clusters. The Hg cluster plasmon maxima and that calculated from Eq. (1) were also found to be well represented by Eq. (2).

In the Drude model of free-electron motion, Γ is related to the mean time τ between collisions by $\Gamma = 1/\tau$ [22]. Taking the experimental value [6] for $\tau(293\text{ K}) = 4.54$ 10^{-16} s one obtains $\hbar\Gamma_\infty$(free electron) $= 1.45$ eV. One calculates $\hbar\Gamma_\infty$(exp) $= 1.33$ eV from Eq. (1) using the experimental dielectric function. This difference is due to the influence of the $5d$ electrons which dampen the free-electron Mie plasmon on the high-frequency side only, leading to a shift of the resonance frequency from 6.12 to 5.73 eV, a narrowing of the plasmon maximum, and a reduction of the $6s$ oscillator strength from 1 to 0.53 [20], in qualitative agreement with the most recent calculation [7].

Figure 4 shows the location of the maxima of the photoabsorption cross sections. The data are plotted as a function of $n^{-1/3}$, a value proportional to the inverse cluster radius. The maxima at high photon energies are nearly independent of cluster size and equal to that calculated for the Mie plasmon. Only a very weak redshift is observed for the three largest cluster sizes ($n = 60$, 80, and 100). We therefore identify this maximum as plasmon absorption. It is surprising that already $Hg_5{}^+$ shows, within experimental error, a maximum at the *same* position as the Mie plasmon. In contrast, the alkali clusters show a blueshift [19], which can be explained as being partly due to a variation of electron spill-out with cluster size [13]. For Hg the ionization energies are much larger, the spill-out thus reduced, and a smaller shift can be expected. Note that singly and doubly charged Hg clusters have the same plasmon energy. The maxima are so broad, however, that the small shift seen for neutral
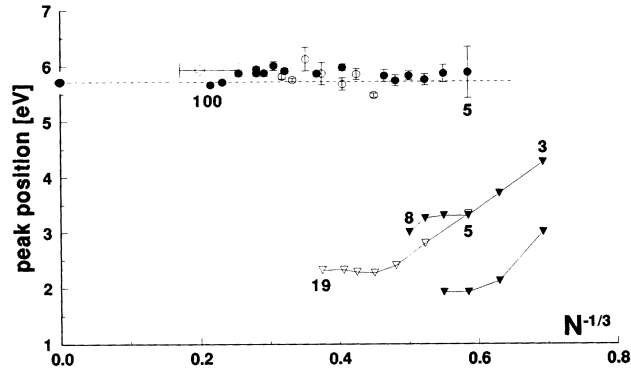
FIG. 4. Positions of the observed maxima are plotted against $n^{-1/3}$. Full (open) symbols refer to singly (doubly) charged clusters. The plasmon peaks are nearly independent of charge state and cluster size, and are equal to the value calculated for the Mie plasmon. The one data point with the horizontal error bar is the result of Ref. [5].

FIG. 5. Full width at half maximum of the plasmon peaks. The one data point with the horizontal error bar is the result of Ref. [5].

and positively charged alkali clusters [12] would not be noticeable.

Metals and metal clusters show a plasmonlike absorption. This had led to the widespread, but erroneous conviction that plasmonlike behavior is confined to metallic systems. Indeed bulk insulators like the alkali halides [25], silicon [26], C_{60} [27, 28], and even xenon [29–31] show both single electron and a plasmon type of absorption. This double-faced behavior follows directly from the linear response theory of the nonlocal susceptibility of a medium due to electronic excitations, which has two contributions, one giving a superposition of single particle transitions, the other a collective plasmon resonance [21, 32].

The width of the plasmon resonances will be discussed now. The relation

$$\Gamma = \Gamma_0 + A\, v_F/R, \qquad (3)$$

where Γ_0 is some intrinsic width, A is a dimensionless constant, and v_F is the Fermi velocity (1.58×10^6 m/s for bulk Hg), is usually used to explain the width Γ of cluster plasmon resonances [33]. A fit of Eq. (3) to the experimental data is given by the solid line in Fig. 5, giving $\Gamma_0 = 0.49 \pm 0.05$ 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 [1] is used to calculate the cluster radius R. The cluster temperature varies by a factor of about 3 between $n = 10$ and 100, as discussed above, and a strong temperature dependence of Γ_0 is conjectured below. Both effects, taken together, will lead to an enhancement of A for clusters having the same temperature. The earliest [34] random-phase-approximation jellium calculation gives $A = 0.2$, while the newest theory [35] gives $A = 0.534$ for the case of Hg. A relation similar to Eq. (3) was derived for
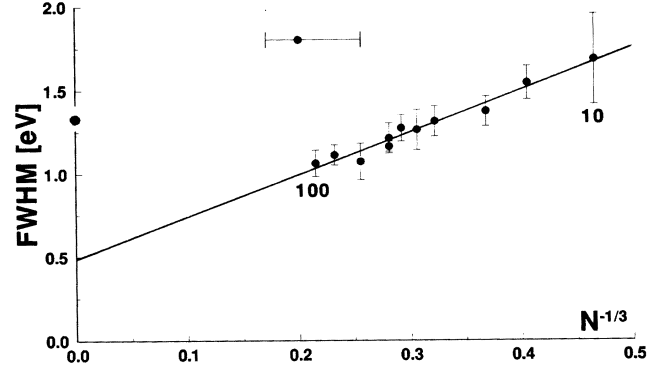
thermally excited clusters [36, 37]; a Gaussian line shape was predicted for this case, but not observed experimentally. A Gaussian fitted to the data of $Hg_{20}{}^+$ (compare Fig. 2) is 30 times lower than the experimental data at 3.6 eV [20].

The relaxation time τ is inversely proportional to the electric resistivity, which thus becomes proportional to the width Γ [24]. A good conductor has a narrow Mie plasmon. The large Hg Mie plasmon linewidth is thus due to the poor electric conductivity of bulk Hg at 300 K. The resistivity decreases by a factor of 16.5 from room temperature to 77 K, and Hg becomes superconducting at 4.2 K [24]. The bulk and large cluster plasmon width can thus be expected to decrease dramatically with temperature.

Note that the solid line in Fig. 5 extrapolates to the "wrong" bulk value. Also all our measured widths are smaller than that of the bulk Mie plasmon. We tentatively explain our extrapolated value of $\Gamma_0 \approx 0.5$ eV as being due to a bulk electric conductivity of Hg at a reduced temperature. If this would be true, the plasmon linewidth could serve as the long sought thermometer for free clusters, at least in the case of Hg.

The width of the plasmon maximum from Ref. [5] is larger by 0.45 eV than the calculated bulk value and 0.75 eV larger than our results in this size range. This is surprising at first, as we see no difference in the width of the singly and doubly charged maxima, so the neutral clusters of Ref. [5] could be expected to be similar. We speculate that this difference is at least partially due to a temperature effect. In the experiment of Ref. [5] the photon beam intersects the cluster beam directly behind the nozzle, where the clusters have had little time to cool. The higher temperature would lead to a larger Γ_0.

In summary, the optical absorption in small Hg clusters shows an abrupt transition to a collective, plasmonlike behavior. The $6s \rightarrow 6p$ transition is no longer visible for $n > 10$ for singly charged clusters. The n value of

this transition is doubled for doubly charged ones. The plasmon energy is nearly independent of cluster size and charge, while the $6s \to 6p$ lines depend strongly on both parameters. The plasmon position is given by the bulk Mie plasmon. The plasmon linewidth is a sum of two terms, a value independent of cluster size Γ_0, for which a strong temperature dependence is conjectured, plus a contribution proportional to the inverse cluster radius. The experimental proportionality constant is bracketed by values from two RPA calculations.

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