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Coulomb staircases and quantum size effects in tunnelling spectroscopy on ligand-stabilized metal clusters

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Abstract. – We describe scanning tunnelling spectroscopy results on the ligand-stabilized metal cluster $Pt_{309}Phen^*_{36}O_{30}$ (where Phen is phenanthrolin) at 4.2 K. If the STM tip is positioned above a single cluster, clear charging effects are observed, varying from a reduction of the current around zero bias (Coulomb blockade) to a stepwise increase of the current as a function of bias voltage (Coulomb staircase). In addition to the regular Coulomb staircase with steps in the current at equal voltage spacing, we observed also staircases whit additional structure. This additional structure can be explained in terms of quantum levels in the cluster.

There is a long-standing interest in the study of small metallic particles because they form the transition between the well-established fields of solid-state physics and atomic physics. Furthermore, these small particles have technical importance, for example in catalysis. Besides the obvious large surface-to-volume ratio, the discreteness of the energy levels (the quantum size effect, QSE) is considered to be the most distinctive property of the particles, which should drastically influence the thermodynamic properties for temperatures that are small compared to the average level splitting. For extensive reviews on the electronic properties of small metallic particles, see the papers by Halperin [1] and Perenboom, Wyder and Meier [2].

One of the main problems in the study of small metallic particles is the spread in size between individual particles. Especially experimental techniques that average over an ensemble of particles suffer from this problem. However, an improvement can be expected from the recently developed ligand-stabilized metal clusters [3]. In these compounds all particles have the same size and geometry. Generally they consist of a core of, *e.g*, Pt, Au, or Pd (with a magic number of atoms of 13, 55, 147, 309, 561,...) surrounded by organic molecules (ligands) that stabilize the structure. One of the main issues of interest in the field of these ligand-stabilized clusters is the question to what degree the core of these large molecules has metallic properties. For a recent overwiev of the physics of this type of clusters, we refer to a paper by de Jongh *et al.* [4].

The tunnelling spectroscopy results we report on are obtained on the cluster $Pt_{309}Phen^*_{36}O_{30}$ (named Pt_{309} hereafter). This cluster consists of a core of 309 Pt atoms, which is surrounded
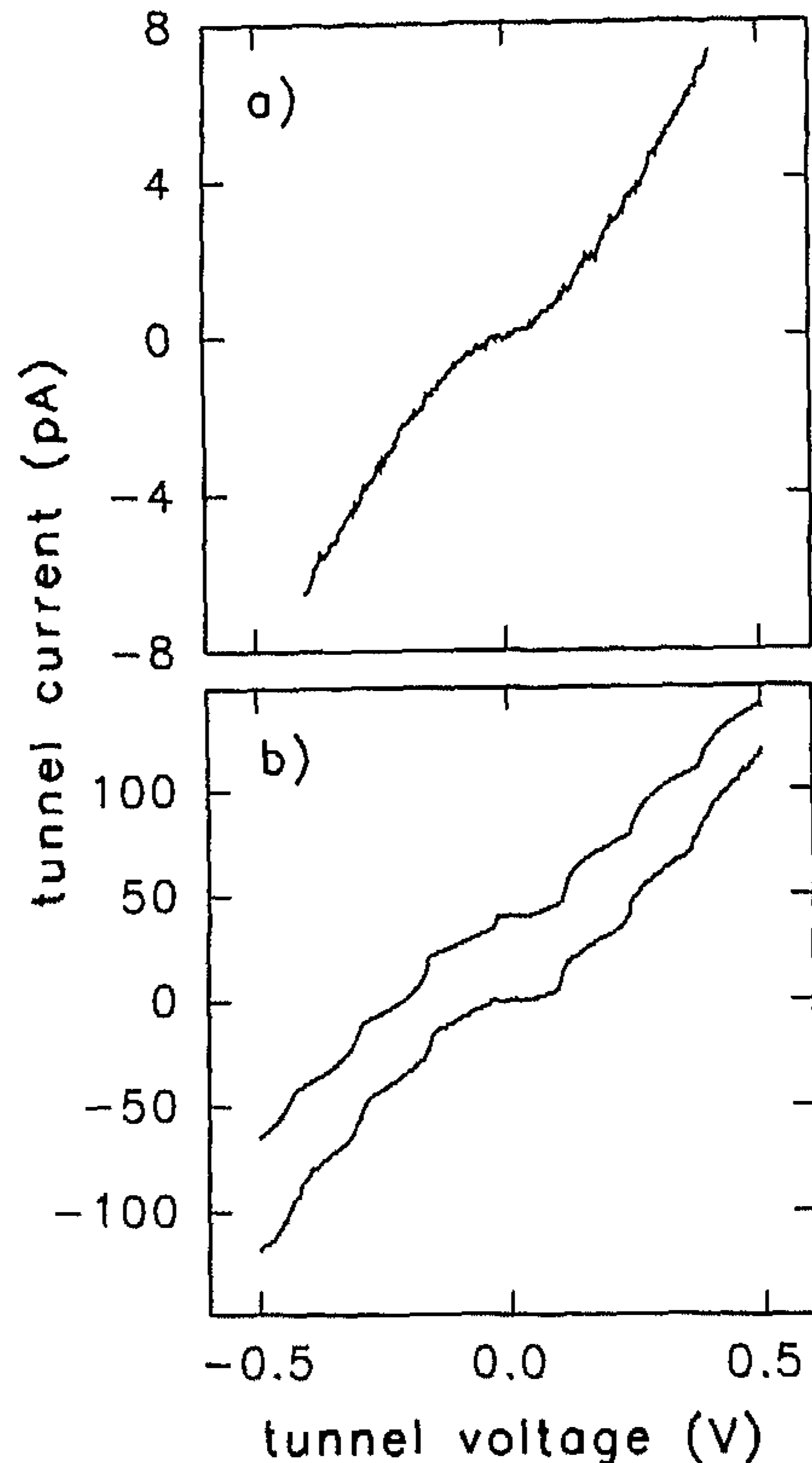
Fig. 1. – Tunnel characteristics on two different Pt_{309} clusters, which both show charging effects. Curve a) only shows a reduction of the current around zero bias (Coulomb blockade). Curve b) shows a Coulomb staircase. The measurement temperature is 4.2 K. The upper curve in b) shows a theoretical curve (offset by 40 pA). The fit parameters for this curve are $C_1 = 1.2$ aF, $C_2 = 0.8$ aF, $R_1 = 4$ GΩ, $R_2 = 0.2$ GΩ, $Q_0 = -0.3$, and the temperature $T = 4.2$ K.

by a ligand shell of phenanthrolin and O_2 molecules. The questions we want to address with the tunnelling experiment are the following. 1) What is the electronic structure of the core of these ligand-stabilized clusters? More specifically: do these clusters show the same charging behaviour as the regular *metallic* particles (see, *e.g*, [5], [6])? 2) Is the layer formed by the ligands suitable to act as a tunnel barrier instead of the normally used oxides? These oxides have impurity levels which may get charged and decharged, giving rise to time-dependent effects (*e.g* [7]), that may obscure features of small energy scales. 3) If the clusters do show the normal charging effects, can we find any indication of the quantum size effect (QSE)? The Pt_{309} cluster has dimensions in which the QSE becomes important at liquid-helium temperatures. Indication for QSE in this compound have been found by nuclear magnetic resonance [8].

The stainless-steel low-temperature scanning tunnelling microscope (STM) used in this experiment has been described elsewhere [9]. All results presented here are obtained at 4.2 K. The tips were made by cutting a 0.5 mm Pt(90%)/Ir(10%) wire with scissors.

The Au[111] substrates are produced by melting gold and cooling it down fast. In this way a gold ball with crystal facets of about 0.5×0.5 mm^2 at its surface is formed. The sample were prepared by depositing a droplet of the solution of the clusters in water on such a facet and blowing it off after a few seconds with nitrogen gas. Topographic images of the clusters were only reproducible at high tunnel resistance (typically 1 GΩ). At low resistances the clusters are easily moved around due to the interaction with the tip [10], [11].

At low temperatures different types of tunnel characteristics are observed above Pt_{309} clusters. All these curves showed clear charging effects. Typical results are shown in fig. 1. In some instances only a reduced current around zero bias is observed (Coulomb blockade, see fig. 1a)) and in other cases a Coulomb staircase (see fig. 1b)). Whether we observed a Coulomb blockade or a Coulomb staircase depended on the ratio of the resistances and capacitances of the two junctions and could almost always be tuned by chancing the distance between tip and cluster (which changes the resistance between tip and cluster). This is in agreement with the orthodox single-electron tunnelling theory, which assumes a continuous density of states for the cluster (see for example [12]). The important parameter is the product of the capacitance and resistance of both junctions. If this product for the junctions is very different ($R_1C_1 \ll R_2C_2$) a Coulomb staircase with sharp steps is expected, whereas junctions with identical parameters ($R_1C_1 = R_2C_2$) show a reduction of the current around zero bias.

The agreement between the orthodox theory and the spectroscopic curves above the clusters show that the electronic structure of the of the cluster core, formed by the Pt atoms, is consistent with metallic behaviour. Furthermore, the observation of clear charging effects on Pt_{309} clusters indicates that the ligands are very good insulators, that in our experimental situation act as a tunnel barrier between cluster and substrate.

We observed a large spread in the charging energy for different tunnel junctions over a range between roughly 50 and 500 meV. This spread in E_c is larger than what one would expect for identical particles. We can estimate the charging energy as $E_c \approx e^2/4\pi\epsilon_0\epsilon_r R$ (with R the radius of the cluster). For a cluster of these dimensions ($R \approx 10$ Å) this estimate gives a value of 140 meV for the charging energy (where we took $\epsilon_r = 10$). However, for this estimate the particle is assumed to be embedded in an infinite dielectric medium with a dielectric constant ϵ_r. In the experiment the thickness of this dielectric medium will be limited by the tunnel barrier width. The correction for this effect is given by a factor $s/(s + R)$, with s the tunnel barrier width [13]. If we take a typical value for s of 5 Å this reduces the value of the charging energy by a factor $s/(s + R) \approx 1/3$. The charging energy that follows from this estimate is about 50 meV. There are several effects that may cause the observed variations in E_c. Since the clusters have different facets (square and triangles) the charging energy will depend on the exact way in which the cluster lies on the substrate. Also the ligands may be oriented differently for the different clusters on the substrate, thus causing a different width of the tunnel barrier between cluster and substrate, and therefore a different capacitance. Another possible reason for the spread in E_c is residual solvent (water) that is frozen on the facet and therefore the tunnel junction between the cluster and the substrate can be completely different for different clusters.

In some instances we observed deviation from a regular Coulomb staircase. This deviation consisted of additional structure on the charging characteristic (see fig. 2). This additional structure can be seen best in the conductance curves of fig. 2b). The following general features were observed for these additional steps. 1) The curves are strongly asymmetric: at negative tip bias the additional structure is much more pronounced and at positive bias additional structure only appears at larger voltages (between 0.2 and 0.3 V in fig. 2b)). 2) The sharpness and presence of the structure is strongly dependent on the tunnel resistance (fig. 2c)). Several effects may cause this more complicated staircase pattern.

First of all, discrete electron levels in the cluster caused by the quantum size effect may cause additional structure on top of the Coulomb staircase. The effect of discrete levels on the charging characteristics has been treated theoretically by Averin and Korotkov [14], Averin, Korotkov and Likharev [15] and Amman *et al.* [16]. In this situation not only steps in the current caused by single-electron charging of the cluster are expected, but also steps associated with the quantum levels in the cluster.
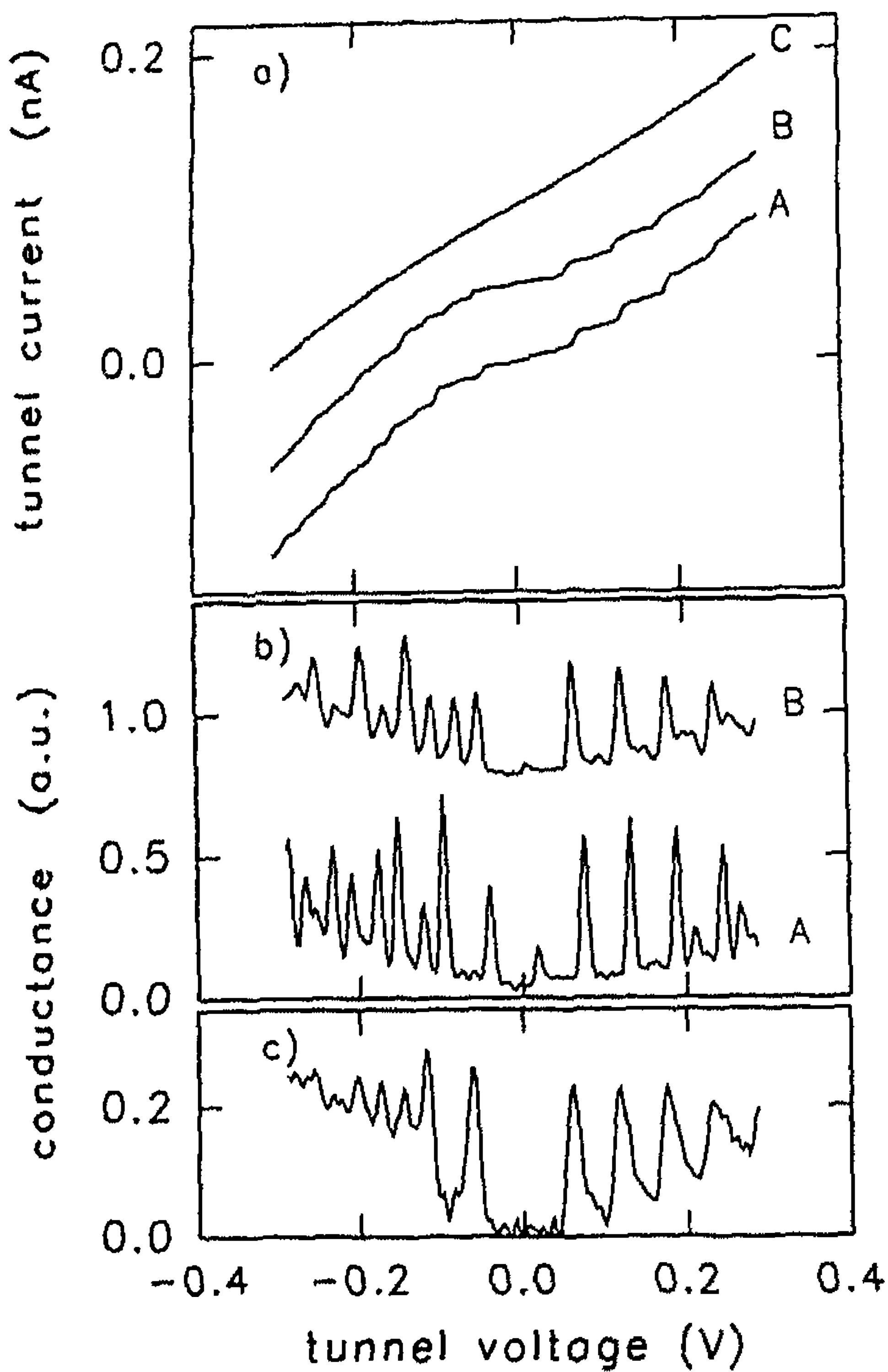
Fig. 2.

Fig. 3.

Fig. 2. - a) Tunnel characteristic above two different Pt$_{309}$ clusters (curve A and B) and above the Au substrate close to the clusters (curve C). The measurement temperature is 4.2 K. In addition to the incremental charging effect there are additional steps resolved. The curve above the bare Au[111] facet shows metallic behaviour. The curves are offset for clarity and have zero current at zero bias. b) Conductance curves for the tunnel junctions above the Pt$_{309}$ clusters. Curve B is offset by 0.75. c) Tunnel characteristic at the same tip position as curve A (a) and b)), but at a different set point value:$V_s = 300$ mV and $I_s = 56$ pA instead of $V_s = 300$ mV and $I_s = 78$ pA (curve A). At this higher resistance the additional steps are less pronounced.
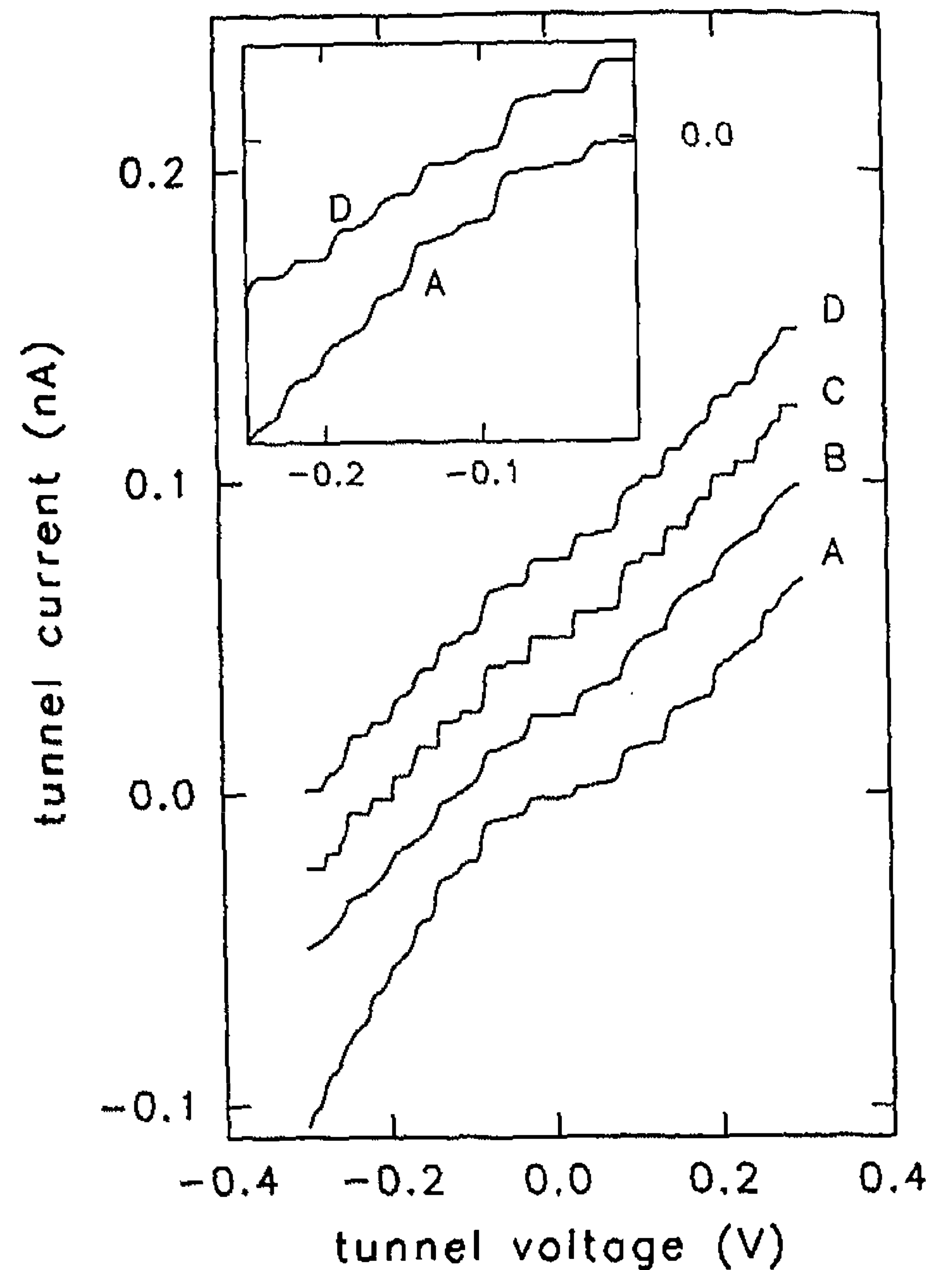
Fig. 3. - Tunnel characteristic obtained above a single Pt$_{309}$ cluster at 4.2 K (A) and three theoretical fits. Curve B is calculated using the orthodox theory without taking into account QSE. The fit parameters for this curve are: $R_1 = 0.2$ GΩ, $R_2 = 3.3$ GΩ, $C_1 = 1$ aF, $C_2 = 2.9$ aF and $Q_0 = -0.01$. Curve C takes into account a level splitting of $\Delta = 21$ meV and the other parameters are the same as for curve B. Curve D has the same parameters as curve C, but is calculated at a higher effective temperature of $T^* = 15$ K. The inset shows the negative bias part of curves A and D. All curves are offset for clarity and have zero current at zero bias.

Figure 3 shows a measured curve (A) and two calculated curves (C,D) that take into account the level splitting according to the theory of Amman et al. [16]. Curve C and D use the same fit parameters, except for the temperature. Curve C use the bath temperature of the cryostat (4.2 K) as the temperature of the cluster, whereas curve D uses higher effective temperature. This higher temperature may originate from the high current densities that are used in an STM experiment. Also given in fig. 3 is a calculated curve for a constant density of state, i.e. without QSE (B). At negative bias the fit with QSE shows the same features as the measurement, whereas at positive bias the curve without QSE is close to the measurement. This difference between positive and negative bias may be caused by a difference in level distribution below and above the Fermi level. Another origin may be that the broadening of

the electron levels due to the tunnel interaction with the substrate is different for levels above and below the Fermi level [14]. This may happen if the tunnel matrix element is different for energies above and below the Fermi level. The level splitting we extract from this kind of fits is rather large compared to estimates. An estimate for the average level splitting, taking into account that the electrons of the outer layer of Pt atoms are bound to the ligands (*e.g.*, [17]), gives $\Delta = 4E_F/3N \approx 8$ meV (where E_F is the Fermi energy of the metal and N is the number of free electrons), whereas the value obtained from fits lies between 20 and 50 meV, where the smaller values are obtained for the cases with a small Coulomb staircase step width. With respect to these values for Δ obtained from fits, it should be noted that there might be an inaccuracy in these values due to the fact that the two capacitors C_1 and C_2 are not known exactly. Namely, due to capacitive division of the applied voltage over the two tunnel barriers, the additional step width will depend, not only on the value of Δ, but also on the capacitors. Therefore, different combinations of the values of C_1, C_2 and Δ, may result in a comparable step sequence. This effect can amount to a maximum of a factor of two, which will occur if the fits assume almost equal values of C_1 and C_2 and the real system has very different values of C_1 and C_2. However, in practice the effect will be smaller since also the Coulomb staircase step are effected by the values of the capacitors and can therefore be used to keep the ratio of the two capacitors within a reasonable range. At first sight, changing the distance between tip and sample might resolve this problem, since this affects the capacitance between tip and sample. However, since the tunnel resistance depends exponentially on this distance and the capacitance only linearly this effect is very weak. This is consistent with the set point dependence shown in fig. 2, where the additional structure, as far as the distance between the conductance peaks is concerned, is the same for the different set points.

Besides the above-mentioned inaccuracy in the determination of the level splitting, several effects may cause the difference between the estimated and experimentally obtained values of Δ. First, it is expected that the level splitting around the Fermi level (which we probe in our experiment) is larger than the average level splitting due to a Jahn-Teller–like distortion [18]. Furthermore, the high symmetry of the cluster is expected to cause degeneracies, thus increasing the level splitting by a substantial amount. This effect is not taken into account in the above-mentioned estimate. The spread in the experimentally obtained values of Δ may have several origins. First, it is possible that the interaction between the cluster and the substrates causes deformation of the cluster core, which results in a lifting of (a part of) the degeneracies. This effect depends on the exact way in which the cluster lies on the substrate and the orientation of the ligands, which brings about that it may be different for different clusters. At this point we note that the additional structure we observed can be fitted accurately by taking into account QSE.

Another possible explanation for the additional steps in a part of the measurements is that we are tunnelling through two clusters instead of one. This might cause the irregular staircase pattern observed in our experiment [19]. Because the topographic scans indicate that we are observing single separate clusters, tunneling through two clusters can only occur if the tip has picked up a cluster during previous scans, which might happen since the clusters are bound loosely to the substrate [11]. However, in this situation we would expect to observe charging effects on the bare gold substrate, which we never did (see fig. 2). This observation makes the explanation of the additional steps by means of a triple-barrier tunnel junction unlikely.

A last origin for the additional structure can be the unknown electronic structure of the ligands. For example, resonant states in these ligands may cause additional structure on the charging characteristic.

Summarizing, we have observed for the first time clear charging effects in tunnelling spectroscopy on well-defined ligand-stabilized metal clusters. This indicates that the nature of the

cluster core of this kind of clusters is consistent with metallic behaviour and that the ligands are insulating. In some measurements additional structure in the charging characteristic was present. This additional structure is consistent with quantum size levels in the cluster. Three junction configurations can produce a similar structure, but can be ruled out on other grounds. A third possible mechanism, resonant tunnelling through states of the ligands, deserves more research.

Additional Remark. – Since the manuscript was submitted an interesting publication on similar measurements has appeared [20]

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