Chemisorption on small clusters: can vertical detachment energy measurements provide chemical information? H on Au as a case study

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Abstract

We present photodetachment spectra of monohydrogenated gold clusters, and investigate the origin of the vertical detachment energies (VDEs) using calculations based on density functional theory. We show that the standard interpretation that associates VDEs to ground-state isomers is not valid. We propose a new one that is consistent with both the most probable formation route and the structure of the parent clusters, and which gives excellent agreement with experiment. We discuss the implications our results have for the interpretation of VDEs when applied to the study of chemisorption in general.

1. Introduction

Determining the structure of a small atomic cluster uniquely is an almost impossible task for experiments alone. Nevertheless a number of sophisticated physical measurements have been used on size-selected clusters to this end. For example, mobility measurements can determine their global shape as proved for aggregates of diverse elements [1,2], and useful information on

their geometry can be provided by photoabsorption and photodetachment spectra, when combined with reliable calculations [3–10]. A related task, at least as ambitious, is that of using these same physical probes to understand cluster chemisorption, namely to identify size effects and especially the most probable chemisorption sites a metal cluster offers to hydrogen, oxygen, or carbon monoxide. Photoelectron detachment has recently been extended to anionic metal clusters with chemisorbed CO [11] and hydrogen [12,13]. However, the power and limitations of this technique to fingerprint reactive sites, also when combined with calculations, are unclear and need to be assessed. This is the purpose of our investigation. The work we present here should clarify

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some of the general – and so far overlooked – problems one encounters when trying to apply such experimental data to the realm of cluster chemistry.

We have chosen an interesting and well-defined system as a case study: hydrogen adsorption on gold clusters. Because of their relevance in newly fabricated, gold-based nanostructured materials (see, e.g., [14,15]), the physical and chemical properties of gold clusters have recently attracted a lot of attention. Anionic clusters (in this case Au_nH^-) are often probed by photoionizing them and by locating in the spectrum the lowest energy peak that corresponds to the binding energy of the ejected electron in the structure of the anion. This is commonly defined as the vertical detachment energy (VDE) and is the quantity targeted by calculations. It is generally compared to values computed for a few isomers, and assumed to identify the ground-state structure of the anion. This quite general assumption is what we are considering here critically in the case of chemisorptive systems. The specific questions we address are: Can we use VDE values to identify where hydrogen preferentially sits? Do they probe the lowest-energy structures? How different is the gold case from that of other metal clusters? As we shall see, a correct interpretation requires the availability of accurate results on a large variety of isomers, not just on a few.

After presenting the experimental spectra, we discuss the results of state-of-the-art calculations based on density functional theory (DFT) performed for a number of cluster geometries. In some cases the measured VDEs clearly indicate high-energy isomers as best candidates. We shall rationalize why this is so on the basis of the computed structural and dynamic properties of the Au_nH^- , by taking into account the special (non-standard) process by which they were generated, i.e., by reacting H ions with gold clusters, and argue that in most cases wherever H^- hits a small gold aggregate, it sticks to it. The isomer thus formed, be it a low- or a high-energy one, produces a signal unless the energy barrier separating it from the ground state renders isomerization a very improbable event.

2. Experimental and computational methods

Gold clusters were generated in a pulsed arc cluster ion source (PACIS) [16]. The target material is eroded and cooled down by interaction with a He buffer, to which hydrogen is directly admixed at high concentration (10–50%). A mixture of gold clusters and atomic hydrogen, in neutral and charged states, enters the extender and cools down to about room temperature. In this way, most of the energy released during the formation process dissipates through interparticle collisions. Neutral gold clusters and hydrogen anions are expected to form with higher probability, and give rise to the hydrogenated gold anionic clusters. This procedure is not commonly used. In other cases studied so far, e.g., H on aluminum [12,13], molecular hydrogen is added to the anionic clusters at a later stage, and, as a result of its dissociation, clusters with more hydrogen atoms are also generated. When this process was applied to gold clusters, however, the signal was extremely weak, suggesting too low a reactivity of small gold aggregates to molecular hydrogen. Photoelectron spectra of mass-selected anions are collected in a ‘magnetic bottle’-type electron spectrometer.

To check the intrinsic reliability of our DFT calculations, we used three different approximations for the exchange-correlation (xc) functionals: the local-density approximation (LDA, [17–19]) and gradient-corrected functionals of the Becke–Lee–Yang–Parr (BLYP, [20,21]) and of the Perdew–Burke–Ernzerhof (PBE, [22]) type, all including spin polarization. PBE results are reported in more detail because this description should be more appropriate whenever both localized and extended electron states are to be correctly treated simultaneously. However, the key findings presented here do not depend on the xc functional. LDA results, although less accurate than those of gradient-corrected xc’s, provide similar qualitative answers. Computational details are the same as in [10,23,24]. Starting from many different configurations, local geometry optimizations were performed followed by vibrational analysis. Car–Parrinello (CP) molecular dynamics (MD) [25] simulations were used to explore the configurational space further, and to investigate the prob-

ability of temperature-induced structural transformations and hydrogen hopping. All results reported here refer to electronic configurations of low spin multiplicity (singlets and doublets) [26].

3. Results and discussion

Fig. 1 shows the photodetachment spectra measured for the Au_nH^- clusters with $n = 2-6$. That of AuH^- extends to lower energies, and the VDE is located at 0.9 ± 0.25 eV.

Fig. 2a illustrates several geometrical isomers of the Au_nH^- clusters ($n = 2-6$), ordered according to their thermodynamic stability (energy difference ΔE to the ground state). All have 2D geometries, as 3D ones are at even higher energies and spontaneously flatten in MD simulations. LDA predicts the same ground-state structure as PBE for neutral and anionic clusters, whereas in BLYP more open structures are sometimes favored (e.g., Au_3H^- and Au_5H^-). This same tendency was pointed out for other elemental metal clusters [10,9]. A detailed discussion of all our findings will be given elsewhere [27].

Fig. 1. Photodetachment spectra of Au_nH^- with $n = 2-6$.

Here we focus on the comparison of calculated and experimental VDEs. As shown in Fig. 2b, VDEs do not correlate with ΔE s, and, depending on the specific size, they may or may not change strongly from one isomer to the other. The extent to which the choice of the xc functional affects the VDE value for a given isomer is within tenths of an eV [27]: more specifically, in most cases gradient corrections tend to decrease it with respect to LDA (by at most 0.3 eV), and PBE and BLYP results agree within 0.1 eV. This is indeed also our experimental resolution, with the exception of AuH^- , where it is lower (0.25 eV).

Fig. 2c illustrates the PBE values of the VDEs versus experiment. Each curve refers to a different choice of the anionic cluster isomer: the ground state, and the one(s) with gold atoms in a structure similar (apart from relaxation) to that of the bare cluster, in either the neutral or the anionic state. The analog BLYP and LDA curves are similar and lead to the same conclusions.

The standard interpretation of the measured VDE [4-8,11-13] (which we call the ‘thermodynamical’ one) associates it to the energy necessary to detach an electron from the anion in its ground state. The values obtained in this way agree well with experiment for $n = 1, 2, 3$, and 6, with a maximum deviation of 0.3 eV (10%), whereas for Au_4H^- and Au_5H^- they are ~ 1 eV higher. The spectra in Fig. 1 show a multitude of signals for both these clusters also in the range $\sim 3.5-4.0$ eV. Why then do we observe well separated and relatively sharp peaks also at lower energies? This picture is not consistent with cases of strong adiabatic effects where broad features are observed. On the contrary, it is more consistent with the coexistence of more isomers. One may be tempted to conclude that, given the complexity of the formation process, all isomers can be observed. This type of interpretation (which we call ‘unselective’), however, is not satisfactory. Provided many possible structures are considered, we will prove that one can trace which ones are responsible for the VDEs measure, following an argument valid for all sizes.

Fig. 2b shows that there are higher-energy isomers with $\sim 0.5-1$ eV lower VDEs: (c) for Au_4H^- and (e) for Au_5H^- . The interesting feature is that

Fig. 2. (a) Structures of several isomers ordered according to the energy difference ΔE with respect to the ground state. (b) Calculated VDEs versus ΔE for all isomers, and (c) selected values from different interpretations (see text) compared to experiment. Dashed lines in (b) correspond to the experimental data.

in both cases the gold core is in the same geometry as in the ground state of the Au_n neutral cluster. If we now assign the measured VDEs to those isomers that are structurally related to the Au_n ones, we find that the agreement is excellent for all clusters considered [see Fig. 2c]. There is a valid

argument in support of this interpretation (which we call ‘parent-related’). In our apparatus, neutral aggregates form with a higher probability than charged ones do, and H is more likely to be present in the anionic than in the neutral form. This suggests that when an H^- hits a neutral gold cluster

(and this is the most probable chemisorption event), it binds strongly, and the newly formed cluster may have a low probability to transform to the ground state. Our results corroborate this picture: (i) The binding energies of these states are high (4–5 eV). The channel $\text{Au}_n + \text{H}^-$ is indeed the one gaining far more energy from the formation of Au_nH^- than $\text{Au}_n^- + \text{H}$ and $\text{Au}_{n-1}\text{H}^- + \text{Au}$ do, namely by more than 1 eV for all n . (ii) The energy barriers for the transformation to the ground state are 1500 K or more. This was verified by explicit energy calculations as a function of suitable reaction coordinates and/or by CPMD runs carried out at high temperatures.

The agreement between theory and experiment found with the ‘thermodynamical’ interpretation for $n = 2, 3$, and 6 is not lost with the ‘parent-related’ interpretation. The isomers corresponding to the two curves coincide for $n = 3$ [Fig. 2c]: Au_3 is a triangle [6,10,28] and the lowest-energy structure of Au_3H^- is also a triangle with H at an atomic site [(a)]. The bridge position [(c) isomer] has a barrier of only 0.01 eV for the hopping of H

to an atomic site. For Au_6H^- , the ground-state and the core-preserving structure are not the same. The former [(a)] is a bicapped square with H on a bridge position, the latter [(b)] has the shape of a triangle [6,27] with H at an apex site. (H at a mid-edge site gives rise to an unstable geometry.) However, their VDEs are the same.

Au_5 has a planar compact structure that can be described as a bicapped triangle [6,10,28]. This core geometry can give rise to six different isomers for a Au_5H^- , depending on where H^- sticks: (a), (b), (d), (e), (g), and (i). Fig. 3 illustrates the distribution of the electron-localization function (ELF, [29]) of the parent Au_5 cluster. The lower the ELF values (they range from 0 to 1), the lower the charge accumulation, hence the greater the electrostatic attraction for an H^- . Therefore, from this point of view, the three nonequivalent atomic sites are equivalent as attraction centers for an H^- , and bridge positions are not significantly dissimilar. However, the final energy differences are not negligible, as shown in Fig. 4, from which one can also deduce the energy barriers needed to transform from one site config-

Fig. 3. Au_5 : contour plot of the electron localization function (ELF). Values increase from 0.00 to 0.45 from black to red.

Fig. 4. Au_3H^- : energetics of different chemisorption configurations. Inset: energy profile of the (e)–(b) transition. Labels correspond to Fig. 2a for the local minima; t^* denotes the configuration at the barrier in the inset.

uration to the other passing through bridge ones. Two isomers are accidentally degenerate and compete for the ground-state structure. The corresponding VDEs are different, but in both cases more than 0.6 eV higher than the measured value of ~ 2.1 eV (first small peak in Fig. 1). The spectrum in Fig. 1 shows a noticeable density in the 2.5–3.0 eV range, into which these and also three other parent-related isomers fall. There is only one out of six whose VDE would fit with the weak peak at ~ 2.1 eV: isomer (e), which is 0.1 eV higher than (a). Its easiest isomerization, which terminates in isomer (b) (shortest hopping distance for H), goes through the t^* configuration and implies a barrier of ~ 1800 K, as shown in Fig. 4 [the inset shows the calculated energy profile plotted as a function of the Au centered angle (reaction coordinate)]. This is the reason the relatively high-energy structure (e) shows up in the spectrum.

Au_4 has two isomers competing for the ground state in either PBE or BLYP schemes: the rhombus and the Y structure (only one of them in LDA) [6,10,28]. The former is preserved in only one isomer of Au_4H^- [(c)], with H at an atom site, because H at a bridge is not a minimum of the potential energy surface. It has a VDE only 0.3 eV higher than experiment and shows high stability in the MD runs at ~ 1000 K. From the Y structure, five out of the six possible isomers are unstable, whereas (b) corresponds to a local minimum of the potential energy surface and does not appear to undergo transformations at least up to 1000 K in our MD runs.

In Fig. 2c we also report the results for another ‘parent-related’ interpretation, with Au_n^- as parents. They become relevant when atomic rather than anionic hydrogen is chemisorbed. Clearly, this formation path is not relevant.

Both Au_2H^- and Au_6H^- have high-energy isomers [(b) and (f), respectively] with VDEs more than 0.5 eV lower than the experimental values. The ‘unselective’ interpretation would not exclude them. Still, we do not observe them. Au_2H^- , with H bridging two gold atoms, turns out to be very stable in our high- T simulations. However, such a structure is highly unlikely to form from either Au_2 or AuH^- . For Au_6H^- , the (f) isomer transforms into the (d) one in MD runs at ~ 100 K. Note that most isomers of Au_6H^- that correspond to metastable states have VDEs within 0.1 eV.

Fig. 1 shows weak adiabatic effects in all cases. This is fully consistent with our parent-related interpretation, which predicts Frank–Condon shifts of at most 0.3 eV. On the contrary, the thermodynamical interpretation yields a strong size dependence and a shift of ~ 0.8 eV for $n = 4$ and 5. Note also that the shape of the large peak observed for $n = 6$ is consistent with the presence of multiple isomers.

4. Conclusions

In this Letter, we have measured photodetachment spectra for clusters obtained from chemisorption of hydrogen on gold, and have been able to provide a consistent interpretation of the measured VDEs. This interpretation is valid for all sizes considered, and is in order with the most probable formation route of the hydrogenated clusters. Our extensive calculations and analysis of the stability of possible configurations reveal that VDEs are not good probes for the energetically favorable chemisorption sites. The threshold of electron detachment pertains to clusters formed from the adsorption of H^- on neutral aggregates, which are the most probable initial components present in the experimental setup. The strong binding energies and the high barriers for hydrogen displacement involved in the structural reorganization to the ground state increase the probability of observing these isomers. This type of energetics may be characteristic of gold and other clusters having a high affinity for hydrogen ions. However, the fact that the formation process rather than the thermodynamics may determine

what is observed is certainly more common, and should be taken into account in any attempt to explain photodetachment data.

However surprising this might be, the thermodynamically favored state was not the one observed and, if one thinks twice about it, there is no experimentally supported reason why the ground state should be the one measured in this case. Indeed, there is currently no clue on how formation takes place, what the specific physical conditions of the system are, and in particular, which time length separates the formation event from the experimental detection. On the other hand, a direct simulation of such processes is out of reach for many reasons. For example, the accurate calculation of free energy barriers is a bottleneck of theory, and, moreover, any attempt whatsoever would be frustrated by the absence of experimental data with which to compare in the case of cluster chemisorption. One reason for the accuracy flaw is the well-known tendency of LDA to underestimate the energy barrier whenever the transition state is more coordinated than either the initial or the final state, and that only a slight improvement can be obtained with gradient-corrected functionals (see, e.g., [30,31]). Our calculations have provided such a semi-quantitative estimate for the energy barriers that supported our findings.

What one can also retain from our experience is that, in general, for adsorbed systems (as well as for clear cases of dissociative addition of H_2 (Pt, Pd, Ni) or CO chemisorption [11,32]), caution must be exercised in ascribing VDEs to ground-state structures and in considering them a test of structure optimizations, as is commonly (and more successfully) done for bare clusters. As we have seen, there may be cases in which different interpretations lead to the same isomer or in which different isomers lead to the same VDE value. Although VDEs cannot be used as fingerprints of preferential chemisorption sites, photodetachment spectra, especially if vibrationally resolved, may still provide interesting information on cluster chemisorption when aided by reliable modeling and simulations.

Further progress in this field will require, from the experimental side, the ability of monitoring the formation process and, from the theoretical side,

the ability of simulating it on the basis of accurate calculations of the kinetics parameters.

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