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Elastic theory of surface deformation in C_{60} adsorption

Andrea C. Levi [a,b,*], Piero Calvini [a,c]

[a] Dipartimento di Fisica, Università di Genova, 16146 Genova, Italy
[b] CNISM, Unità di Genova, Italy
[c] Istituto Nazionale di Fisica Nucleare, Sezione di Genova, Italy

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Abstract

In molecular physisorption, beyond attractive and repulsive forces, a third contribution arises from the elastic deformation of the surface. In this paper the *dimple* appearing on a gold surface upon physisorption of a C_{60} molecule is studied and its effect on the adsorption energy is evaluated.

The depth and shape of the dimple are studied on the basis of the theory of elasticity. The equilibrium equation is solved in the presence of the body forces originating from a suitable Au–C_{60} interaction potential and the solution for the deformation field is obtained by means of a two-step procedure. In the first step a curl-free deformation field is obtained, which takes the effects of the body forces into account, but generates mismatch of the boundary conditions. In the second step the solution of the equilibrium problem in the absence of body force is generated, which compensates the previous boundary condition violation. Thanks to linearity, the final solution is obtained as the sum of the results of the two steps. An (approximate) iterative scheme is applied for taking the surface deformation into account in imposing that no forces act on the Au surface.

When the distance z_0 of the centre of the C_{60} cage from the surface is rather large, the *dimple* is represented by a bulging surface, but, as the C_{60} approaches the Au surface, the surface recedes and a well formed dimple appears. The corresponding depth at the mechanical equilibrium position ($z_0 = 4.8$ Å) turns out to be 36.3 pm.

Keywords: Physical adsorption; Metallic surfaces; Gold; Fullerenes

1. Introduction

Surfaces, as is well known, may change drastically when foreign atoms or molecules are adsorbed on them. Most such changes are typical of chemisorption and, indeed, chemical in nature: such changes may involve a thorough reconstruction of the surface. Less well known are the effects of physisorption; since by definition in this case no chemical process takes place, the effects reduce to a mechanical deformation [1], and can be described in terms of forces acting on all the atoms or ions in the crystal (of course mostly near the surface location of the adsorbed molecule).

In the latter case the most probable surface deformation involves the formation of a *dimple* (by other authors called *pit* [2] or *calyx* [3] or *trench* [4]): the attractive forces favour the molecule to approach the surface as much as possible, while in turn, under the effect of the repulsive forces, the surface retreats. The above attractive and repulsive forces, as well as the stresses within the crystal due to the surface deformation, determine the equilibrium position of the adsorbed molecule and the depth of the resulting dimple [1]. It is important to distinguish two cases: reversible vs. irreversible dimples. In the reversible case the dimple disappears as soon as the molecule is removed; in the irreversible case, on the other hand, the surface restructuring persists under removal of the foreign molecule. The latter case is more

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[*] Corresponding author. Address: Università di Genova, Dipartimento di Fisica, via Dodecaneso 33, I-16146 Genova, Italy. Tel.: +39 010 3536200; fax: +39 010 311066.

E-mail address: levi@fisica.unige.it (A.C. Levi).

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difficult to model theoretically, but easier to see experimentally, since the surface can be unequivocally visualized in the absence of foreign molecule perturbations [4].

The dimple formation is interesting in itself, but may also lead to interesting applications, such as nanostructuring of a surface using e.g. a regular array of adsorbed molecules. If this could be performed irreversibly, the surface might be cheaply nanostructured to some desired arrangement in very precise and microscopic detail.

In a previous, introductory work [1], we studied the physisorption of CH_4 on both Au and solid Ar. Methane was chosen for two reasons: (a) it interacts weakly with most surfaces, representing thus a relatively clean physisorption case; (b) it is highly symmetrical, so that (ignoring tetrahedrical details...) a spherical approximation appears to be reasonable. It is clear, however, that really interesting dimples can be generated only by molecules interacting more strongly with surfaces. The present work deals with the important case of C_{60}, where point (b) still holds: in fact, this molecule is much closer to a sphere than CH_4 and spherical symmetry will be assumed throughout.

It must be stressed that large molecules (typical size, tens of Ångströms) interacting with metal surfaces can often form strong chemical bonds, anchoring to the topmost layers and restructuring the surface. Still several questions remain unanswered, such as which part of the large molecule interacting with the surface plays the dominant role in the bond and under which conditions the molecular anchoring induces surface restructuring. Moreover, with many metal surfaces, C_{60} shows charge transfer effects. Although we hope to consider such difficult questions in future studies, in the present article we restrict ourselves to the adsorption of C_{60} on gold, where all such effects should be absent, or at least less relevant.

Very interesting, for our present purposes, is the restructuring observed in the beautiful X-ray experiment of Pedio et al. on the adsorption of C_{60} on Au(110) [2], where a dimple, or *pit*, is clearly visible. This experiment was discussed theoretically, via an *ab initio* calculation, by Baxter et al. [3], who compared the structure proposed by Pedio et al. with a different structure proposed by Gimzewski et al. [5] (Baxter et al. compute, in particular, the structure obtained in [2] as it would appear in an ideal case, and show how it gets partly blurred and smoothened when disorder is included by optimization [3]). A similar situation has been found by Weckesser et al. on Pd(110) [6]. On the other hand a very anisotropic, irreversible dimple has been observed by Schunack et al. [4] in the adsorption of hexa-tert-butyl-decacyclene on copper.

In the present article the dimple appearing in a gold surface upon C_{60} adsorption is studied, and its effect on the total adsorption energy is calculated. As in [1], we call **R** the distance vector parallel to the surface (from an origin directly below the centre of the C_{60} ball), and $\zeta(\mathbf{R})$ the local perpendicular displacement of the gold surface with respect to the undeformed surface plane, a dimple corresponding to predominantly negative values of ζ.

To compute the dimple shape and depth we must consider the different energy contributions occurring in the physisorption problem:

(a) the *attractive energy*, essentially due to van der Waals forces (the possible effect of Coulomb interactions will be briefly considered at the end of the paper);
(b) the *repulsive energy*, due to the Pauli principle;
(c) the *elastic energy*, resisting deformation within the metal.

2. Attractive energy

As we will see later, the Coulomb interactions have little or no influence on the effects discussed in the present work; accordingly, only van der Waals attractions will be considered here. Attractive forces will thus be treated summing (or rather, in a continuum picture, integrating) $-C_6 r'^{-6}$ contributions from van der Waals interactions between an individual carbon atom and a gold ion at a distance r' from it. The sum over carbon atoms is performed on the C_{60} surface (treated as spherical). In the continuum picture the carbon atoms are replaced by a uniform carbon surface density ρ_C on the sphere, so that the potential acting on a gold ion placed at a distance r from the centre of the molecule is given by

$$W_a(r) = \rho_C \int V_a(\theta,\phi)\mathscr{R}^2 \sin\theta \, d\theta \, d\phi. \tag{1}$$

Here $\mathscr{R}$ is the C_{60} radius (3.55 Å), $\rho_C = 60/(4\pi\mathscr{R}^2)$, and the potential $V_a(\theta,\phi)$ depends only on the distance r' between the gold ion and a carbon atom placed at the coordinates (θ,ϕ) on the C_{60} surface:

$$V_a(\theta,\phi) = -\frac{C_6}{[r'(\theta,\phi)]^6}. \tag{2}$$

The integral gives

$$W_a(r) = -\mathscr{K}_6 \frac{r^2+\mathscr{R}^2}{(r^2-\mathscr{R}^2)^4}, \tag{3}$$

where $\mathscr{K}_6 = 60C_6$.

This potential $W_a(r)$ is then to be integrated over the volume of the metal. Assuming the C_{60} ball to be centred at $(0,0,z_0)$, the attractive energy is given by

$$E_a = \rho_{Au} \iint dx\,dy \int_{-\infty}^{\zeta(x,y)} W_a([x^2+y^2+(z_0-z)^2]^{1/2})\,dz, \tag{4}$$

where ρ_{Au} is the ion number density in the crystal. In the absence of a dimple, i.e. for $\zeta(x,y)=0$, E_a reduces to

$$E_a = -C_3 \frac{z_0}{(z_0^2-\mathscr{R}^2)^2} \tag{5}$$

with $C_3 = 10\pi\rho_{Au}C_6 = \pi\rho_{Au}\mathscr{K}_6/6$.

Actually, the attraction should be split into two terms. To the contribution given by (3) and (4), due to the ions, a contribution from the valence, quasi-free electrons should