

Charge transfer and adsorption energies in the iodine–Pt(1 1 1) interaction

Alexandre Tkatchenko, Nikola Batina, Andrés Cedillo, Marcelo Galván *

*Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana—Iztapalapa,
Av. San Rafael Atlixco 186 Col. Vicentina, AP 55-534, México DF 09340, Mexico*

Received 26 July 2004; accepted for publication 18 February 2005

Available online 10 March 2005

Abstract

The adsorption energies for iodine atom on the fcc, hcp, bridge, and atop sites of the Pt(1 1 1) surface were determined using ab initio DFT method in two different unit cells. A periodic slab model is used and the obtained energies are in agreement with the corresponding experimental values extrapolated at 0 K. The charge transfer is determined by the use of the Hirshfeld partitioning scheme, and the charge transfer values follow the adsorption energy trend for different sites of the Pt(1 1 1) surface. The results show that the plane-wave DFT approach correctly describes the adsorption of iodine on the Pt(1 1 1) surface and support the use of the Hirshfeld method in surface science problems.

© 2005 Published by Elsevier B.V.

Keywords: Pt(111); Hirshfeld partition; Charge transfer

1. Introduction

The adsorption of iodine on Pt(1 1 1) surface has been studied extensively by many experimental techniques [1–8] but only a very few theoretical ab initio studies exist on the subject [9,10]. The interest in this system can be explained by the fact that the experimental procedures for its prepara-

tion and characterization are well established, yet it presents a structural richness, having four distinct structural phases at different coverage: $(\sqrt{3} \times \sqrt{3})R30$, $(\sqrt{7} \times \sqrt{7})R19.1$, (3×3) -sym. and (3×3) -asym., each of them is characterized by one or several specific adsorption sites [1,5,6]. Also, same results are obtained in vacuum, air and solution environments [7]. Although the experimental results on this system are very convergent, many answers remain to be obtained from theory related to its chemistry and structural arrangement. For instance, the nature of I–Pt bond for different adsorption sites, Pt surface

* Corresponding author. Tel.: +52 55 58046413; fax: +52 55 58046415.

E-mail address: mgalvan@xanum.uam.mx (M. Galván).

relaxation, and stability of different structural phases remain as unexplained issues in this system from the theoretical point of view. The present work concentrates on some of these problems. Majority of the previous ab initio studies have treated the three-fold hollow site for the adsorption of halogens on metal surface [10]. Therefore, it is important to investigate a variety of possible adsorption sites in order to give a richer description of the substrate–adsorbate systems. Consequently, four different adsorption sites were chosen for testing in this case: fcc, hcp, bridge and atop, see Fig. 1.

In order to study the charge transfer occurring between iodine atom and the surface, the Hirshfeld atoms-in-molecules stockholder partitioning (HAMSP) scheme was applied [11]. A recent rationalization of this scheme due to Nalewajski and Parr gives insights of the physical grounds of this partitioning scheme [12]. In addition, for molecular systems, the HAMSP procedure provides an almost basis independent qualitatively description [13,14]. In particular it is quite useful when non-localized basis sets are used because charge transfer can be obtained straightforwardly by integration of the fragment densities in the unit cell.

One of the goals of the present work is to address the charge transfer description of the fcc, hcp, bridge and atop positions for iodine adsorption on a Pt(111) surface periodic slab model. Charge transfer is measured according to the

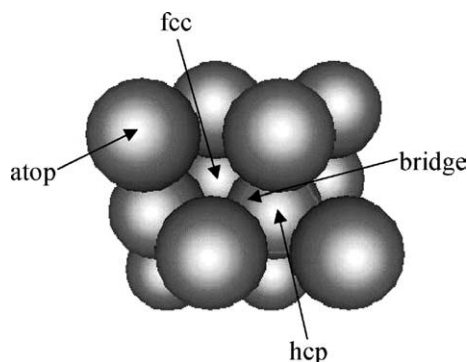


Fig. 1. Top view of the unit cell of the three layers slab model for Pt. Arrows indicate the iodine adsorption sites.

HAMSP prescription. Additionally, an estimation of the adsorption energies on those sites is provided at the GGA/DFT level of theory and their relation to the charge transfer is discussed.

2. The Hirshfeld stockholder partitioning scheme [12]

The electron density of the adsorbed iodine atom on the surface, $\rho_{\text{IS}}(r)$, is represented as the sum of two fragment densities, $\rho_{\text{S}}(r)$ and $\rho_{\text{I}}(r)$, with electron numbers, N_{S} and N_{I} . These electron numbers are different from the electron numbers of the isolated fragments, N_{S}^0 and N_{I}^0 , but they still sum to the total number of electrons of the system: $N_{\text{I}} + N_{\text{S}} = N_{\text{IS}}^0 = N_{\text{I}}^0 + N_{\text{S}}^0$. In this context, the *promolecule* density is defined as,

$$\rho_{\text{IS}}^0(r) = \rho_{\text{S}}^0(r) + \rho_{\text{I}}^0(r), \quad (1)$$

where $\rho_{\text{S}}^0(r)$ and $\rho_{\text{I}}^0(r)$ are the densities of the isolated fragments.

The entropy deficiency (missing information) functional for the above system is

$$\Delta S[\rho_{\text{I}}, \rho_{\text{S}}; \rho_{\text{I}}^0, \rho_{\text{S}}^0] = \int \rho_{\text{I}}(r) \ln \frac{\rho_{\text{I}}(r)}{\rho_{\text{I}}^0(r)} dr + \int \rho_{\text{S}}(r) \ln \frac{\rho_{\text{S}}(r)}{\rho_{\text{S}}^0(r)} dr, \quad (2)$$

and the minimum entropy deficiency principle applied to the above functional gives

$$\delta \left\{ \begin{array}{l} \Delta S[\rho_{\text{I}}, \rho_{\text{S}}; \rho_{\text{I}}^0, \rho_{\text{S}}^0] + \lambda(r)(\rho_{\text{I}}(r) \\ + \rho_{\text{S}}(r) - \rho_{\text{IS}}(r)) + \lambda_{\text{I}}(\int \rho_{\text{I}}(r) dr - N_{\text{I}}) \\ + \lambda_{\text{S}}(\int \rho_{\text{S}}(r) dr - N_{\text{S}}) \end{array} \right\} = 0. \quad (3)$$

The function $\lambda(r)$ is a local Lagrange multiplier for the restriction

$$\rho_{\text{I}}(r) + \rho_{\text{S}}(r) = \rho_{\text{IS}}(r), \quad (4)$$

whereas λ_{I} and λ_{S} are related to the normalization of $\rho_{\text{I}}(r)$ and $\rho_{\text{S}}(r)$, respectively. Eq. (3) can then be transformed into an equation for the fragment densities,

$$\sum_{\alpha=\text{I,S}} \left\{ \ln \left[\frac{\rho_{\alpha}(r)}{\rho_{\alpha}^0(r)} \right] - \ln D(r) \right\} \delta \rho_{\alpha}(r) = 0. \quad (5)$$

The term $\ln D(r)$ includes the Lagrange multipliers, $\lambda(r)$, λ_I and λ_S . The two terms in curl brackets allow to conclude that

$$\rho_\alpha(r) = \rho_\alpha^0(r)D(r); \quad \alpha = I, S. \quad (6)$$

Eqs. (4) and (6) imply that

$$D(r) = \frac{\rho_{IS}(r)}{\rho_{IS}^0(r)} \quad (7)$$

Finally one can get the “stockholder” partition as:

$$\begin{aligned} \rho_\alpha(r) &= w_\alpha(r)\rho_{IS}(r) \\ w_\alpha(r) &= \frac{\rho_\alpha^0(r)}{\rho_{IS}^0(r)}; \quad \alpha = I, S. \end{aligned} \quad (8)$$

The local quantities $w_\alpha(r)$ are sharing factors that determine the relative share of fragment α in the *promolecule* density $\rho^0(r)$. The fragments defined by the stockholder partition are open regions with effective charges generally different from the free fragments. Such differences are caused by the charge transfer component of the chemical bond. On the practical side, it has been shown that the Hirshfeld prescription provides fairly transferable charge distributions and moments and it is largely insensitive to the basis set [13,14].

In the particular case of solid state methods, the HAMSP charges can be obtained by integration of the fragment densities in the unit cell volume.

3. Methodology

The surface models used in the present work are slabs that include five layers of four Pt atoms each perpendicular to the (111) direction with iodine atoms adsorbed on both sides of the slab to eliminate the dipole moment in the unit cell. They correspond to a (2×2) and (3×3) surface models with coverages of 1/4 and 1/9 respectively. The I–I distances for these models are of 5.55 Å and 8.325 Å respectively; even in the (2×2) model the I–I distance is greater than twice the van der Waals radius of iodine atom which is of around 2.2 Å indicating that one should expect a weak interaction between neighboring iodine atoms for both models. The electronic structure was calculated within the Kohn–Sham DFT formalism [15] using LDA and PBE exchange and correlation functionals [16].

The Kohn–Sham equations were solved using a plane wave expansion truncated at 40 Ry within the DFT++ program [17]. The core electrons were not treated explicitly and norm conserving pseudopotentials were used. Trouillier–Martins type pseudopotentials [18] were designed for each type of functional. It is well known in the literature [19] that LDA gives better geometry and GGA gives better description of energies for the Pt(111) surface. According to those findings, by using the LDA formalism the lattice parameters for the bulk and (111) surface were in good agreement with the reported experimental values [20]. For the GGA calculations the lattice parameter for bulk and the bulk modulus were in agreement with other GGA studies, with the bulk lattice parameter slightly overestimated by 2% from the experimental value [19]. Therefore, an optimized value of the platinum lattice constant was used in surface calculations for each kind of functional: 3.92 Å for LDA and 3.99 Å for GGA. The use of 8 and 4 k -points in the irreducible Brillouin zone for (2×2) and (3×3) cells respectively was determined as appropriate to converge the total energy up to 1 mhartree. Therefore, these sets of k -points were used throughout this study. The supercell includes a vacuum region equivalent to 6 layers of Pt atoms. The truncation of up to 40 Ry assures a convergence in the energy that is even better than the one obtained for the k -point sampling. The geometry of the I–Pt(111) system with iodine adsorbed on fcc, hcp, bridge and atop sites, was relaxed at the LDA and GGA–PBE levels of theory. The forces on the atoms in the unit cell were reduced up to 10^{-3} hartree/bohr. In order to calculate the effective charges of the fragments defined by Eqs. (8), we used the same numerical grid that is used to manage the density in the DFT++ code, to integrate the fragment densities in the unit cell. Besides the calculation of the isolated iodine atom, which was done using the spin-polarized method, all the calculations were done with the spin restricted formalism. For the isolated atom calculation the characteristics of the unit cell, k -point sampling and energy cutoff were the same as those used for the complete surface model. The energy of an isolated iodine atom was obtained by a spin-polarized calculation in a large cell.

4. Results

Table 1 shows the iodine–surface equilibrium Z distance, charge transfer and adsorption energies for fcc, hcp, bridge and atop adsorption sites. In relation to the iodine–surface distances reported in Table 1, one may say, for the case in which the experimental value is known, that the calculated LDA value is in good agreement with experiment [4–6]. In all the cases, the Z distance value is calculated with respect to the first Pt layer of the surface. The order in the perpendicular distance is as expected fcc \approx hcp < bridge < atop. The GGA optimized iodine–surface distances are larger than for LDA as it is expected, but the GGA trend follows LDA results. The adsorption energies, obtained at the GGA level relaxing the lattice parameter and the geometry inside the unit cell, follow a standard trend which is inverse to the order of distances; in relation to the adsorption energy it is important to mention that previous calculations in the literature, based on finite cluster approach, reported values [10] that are off by more than 50 kcal/mol (120 kcal/mol) whereas our estimation for the fcc adsorption in the (3×3) cell differ only by 4 kcal/mol (65 kcal/mol) from the corresponding 0 K extrapolated value [8]. The above results show that the adsorption model and calculation approach is the most reliable used up to now to treat this system.

In order to determine the magnitude and the mechanism of the charge transfer process between iodine and the surface, one may divide the effects in global and local. The former deals with the net charge transfer effects calculated as the differ-

ence $N_\alpha - N_\alpha^0$; the quantity N_α is calculated by integration of Hirshfeld fragment densities $\rho_\alpha(r)$ in the unit cell volume. Such differences are reported in Table 1 for the GGA case but LDA results show a similar qualitatively behavior. In contrast with previous theoretical approaches, the electron charge is transferred to the Pt(111) surface when iodine is adsorbed on it, except for the atop site where iodine atom has a very small charge. There is a clear tendency in the charge transfer, the stronger interaction, measured in terms of adsorption energies, the larger the charge transfer. In the atop adsorption site the transfer has the lowest absolute value, and the order in the amount of transferred charge from the iodine atom to the surface is fcc > hcp > bridge > atop. Experimental evidence indicates that upon adsorption a small charge is left on the iodine atoms [7]. This fact can be related to our findings and is further supported by the agreement in adsorption energies between our study and TPD experiments [8], although such a comparison is not straightforward due to different contributions to the charge transfer in electrochemical experiments.

The local charge transfer effects can be analyzed by using the density difference, $\Delta\rho(r) = \rho_{\text{IS}}(r) - \rho_{\text{IS}}^0$. The positive values of this difference indicate the regions where accumulation of electron charge occurs due to the iodine–surface interaction; similarly, the negative regions are related to depletion of the electron charge. Figs. 2 and 3 display the total density, $\rho_{\text{IS}}(r)$, and the density differences for both the fcc and atop adsorption sites respectively. In the case of the fcc site, the I–Pt bond can be observed in the density difference plot as a pale

Table 1
Charge transfer, equilibrium positions of iodine and adsorption energies for different sites on the Pt slab

Site	Eq. position in (2×2) LDA (\AA)	Eq. position in (2×2) GGA (\AA)	(2×2) I–Pt charge transfer ^a	(3×3) I–Pt charge transfer ^a	Adsorption energy in (2×2) cell (kcal/mol) ^a	Adsorption energy in (3×3) cell (kcal/mol) ^a
fcc	2.14 (2.09–2.17) ^b	2.19	0.08	0.13	61.3	64.5 (61.0) ^c
hcp	2.15	2.20	0.08	0.12	60.9	64.1
bridge	2.23	2.30	0.05	0.10	59.3	60.6
atop	2.53	2.59	–0.02	–0.02	51.7	52.2

^a GGA calculations.

^b Experimental values taken from Ref. [6].

^c Extrapolated experimental value at 0 K; Ref. [8].

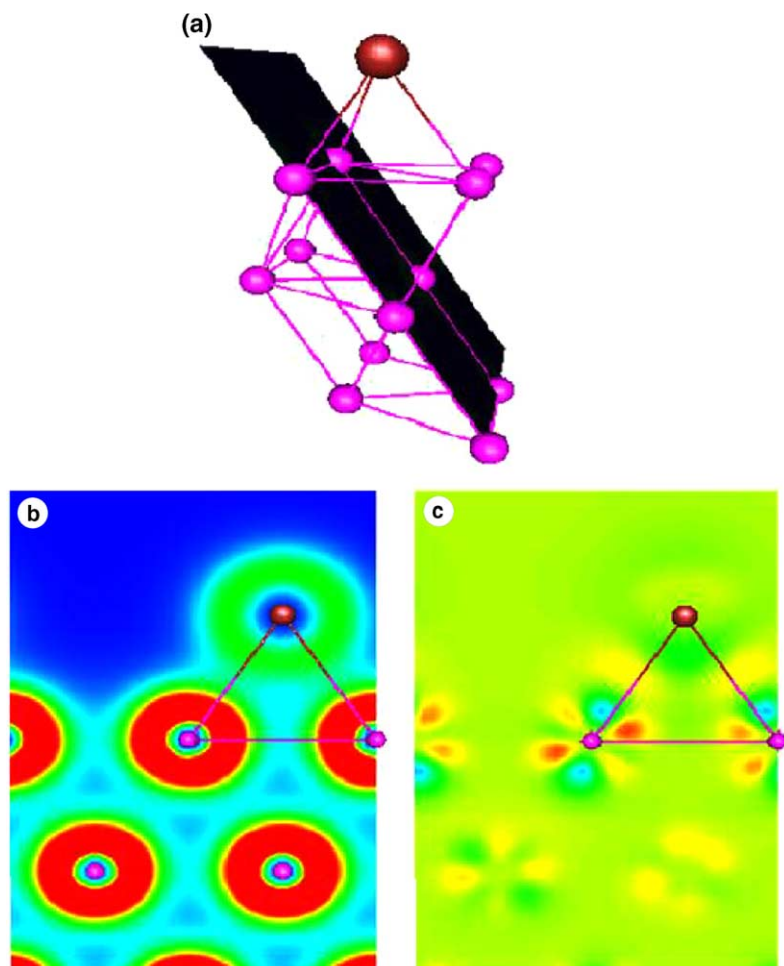


Fig. 2. (a) Unit cell; (b) total density and (c) density difference, $\Delta\rho(r)$, for I–Pt(111) in the fcc site of the (2×2) cell. Only three of five layers of the Pt slab used in simulation are shown along with iodine adsorbed on one side of the slab. The plane in both figures crosses iodine and two surface Platinum atoms as indicated in panel (a); to clarify this point one has to recall that the periodic image of iodine atom in the neighbor cell to the left of the figure will sit on the plane. The scale goes from blue (minimum) to red (maximum); purple spheres indicate atom positions. The total density is a positive definite quantity therefore, in this case the scale goes from 0 to 0.39 a.u. The density difference scale goes from -0.056 to 0.027 a.u with red and yellow indicating positive values and the blue and green regions the negative ones.

yellow region between them; and for the atop adsorption site this bond is represented by a pale red region. These density differences in both sites show strong effects in the first layer of platinum. Also, for both adsorption sites there are charge depletion regions (blue–green) with a p-orbital shape around the Pt atom; which have companion accumulation regions (red–yellow) with d-orbital shape. These combination of regions suggests a

sort of retro-coordination scheme in which the Pt atoms of the first layer interacting directly with the iodine atom donate electrons to the bonding region and simultaneously take out electrons from the adsorbed iodine, finally localized in the empty d-states. Depending on the adsorption site, both effects have a net balance favorable towards charge transfer to the platinum surface for fcc, hcp and bridge sites but they give rise to a slightly opposite

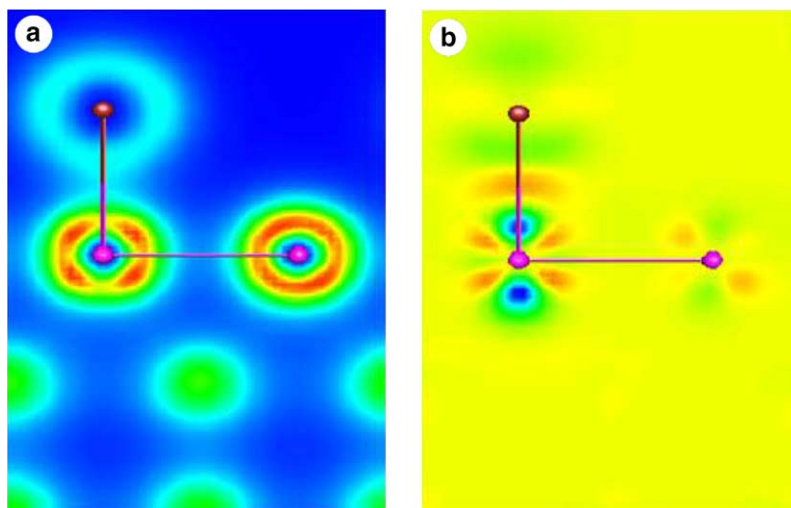


Fig. 3. (a) Total density and (b) density difference, $\Delta\rho(r)$, for I–Pt(111) in the atop site as obtained for the (2×2) cell. The plane in both figures crosses iodine and one surface platinum atom along the (111) direction. The scale goes from blue (minimum) to red (maximum); purple spheres indicate atom positions. For the total density the scale goes from 0 to 0.39 a.u. The density difference scale goes from 0.078 to 0.029 a.u. with red and yellow indicating positive values and the blue and green regions the negative ones. In this case the yellow background corresponds to value close to zero.

charge transfer for the atop site. The order of magnitude of the adsorption energies indicates a strong covalent interaction between iodine and the surface, and from the values of Table 1 one may say that the interaction on atop site is the less ionic and the ionic character has the order $\text{fcc} \approx \text{hcp} > \text{bridge} > \text{atop}$.

By comparing the results obtained for the (2×2) and (3×3) models (see Table 1) one may say that, whereas the charge transfer for the atop site is not sensitive to the degree of coverage, there is an increase in the amount of charge transferred to the surface for the other three sites when the degree of coverage is reduced; the equivalence in charge transfer between the fcc and hcp sites for the (2×2) model is lost by a small amount in the (3×3) model. It is important to notice that, at least for the two studied cases, a decrease in the degree of coverage is related to a larger charge transfer from iodine to the surface for the fcc, hcp and bridge sites. This behavior can be explained in terms of the maximum amount of charge the surface can take from an iodine adlayer. More atoms in the iodine adlayer yield a smaller charge transfer per iodine atom. A similar pattern is observed for

the adsorption energies: in going from the (2×2) to the (3×3) model, the similarity between fcc and hcp is maintained within 1 kcal/mol and the bridge site has smaller value; this last difference is enhanced in the (3×3) model to become of the order of 4 kcal/mol; the atop site remains, for both models, as the site with the lowest adsorption energy.

In order to test if the dipole, induced by a single side adsorption model, has some influence on the energy and charge transfer we repeat the calculation for the fcc adsorption site in the (3×3) cell model with iodine atom adsorbed on one side of the slab. The charge transfer is affected in the order of 0.001 electrons and the adsorption energy on the order of 0.3 kcal/mol, both values are not significant for the level of theory presented here.

5. Discussion

With respect to the charge transfer direction, all previous studies reported charge donation from the Pt surface to iodine atom, which is opposite to our findings. More striking is the fact that in

previous reports the adsorption energies are off by 60 kcal/mol [10]. In contrast to the differences mentioned above, the iodine–surface distance on the fcc site in this work is in good agreement with all previous experimental and theoretical data. It is also important to remark that all previous studies were based on the finite cluster approach using localized basis sets, with clusters ranging from 3 to 12 Pt atoms [9,10]. In order to see the impact of using a finite cluster model in comparison with our approach, we have also done calculations with a 10 atoms Pt cluster and an iodine atom adsorbed on the fcc site, since this model is the most frequently used in previous studies. Very high spin contamination was found in the localized basis set calculations. In our case only the isolated iodine atom requires the use of the spin polarized method. Another source of these differences is related to the fact that the cluster approach corresponds to the limit of very low degree of coverage. The differences observed in the adsorption energy between the cluster approaches and our work could be related to a combination of such effects. The experimental results always imply a certain degree of coverage, which is closer to the models used in this work than to the isolated limit of the cluster approaches. Consequently, the agreement of our results with experimental data obtained in TPD and LEED studies indicate that the use of slab models are more suitable for studying such systems.

In the earlier experimental studies, one could find a lot of speculation about the covalent nature of the iodine–surface bond [3,7], our results definitely confirm this fact. It is also clear from our density difference analysis that the interaction between iodine and the Pt surface atoms can not be associated to the van der Waals forces.

The Hirshfeld partitioning scheme used here gives qualitatively results which are equivalent to other methods for obtaining subsystem charges such as Mulliken [21] population analysis and Bader's AIM scheme [22]. Hirshfeld charge transfers are usually smaller than those obtained by standard population analysis; however, a good qualitative description is obtained regardless of the basis set used [13,14]. This partitioning scheme has been successfully used in studies concerning

molecules, but we believe it could be of major help for studying charge transfer processes in surface science, particularly when non-localized basis sets are used, because it is quite straightforward to implement. In our particular case, Hirshfeld scheme seems to give very consistent charge transfer results as compared to the adsorption energy trends obtained.

Density difference $\Delta\rho(r) = \rho_{\text{IS}}(r) - \rho_{\text{IS}}^0$ is the recurrent quantity used to determine the charge transfer in plane-wave studies [23]. From Hirshfeld fragment densities, it can be easily seen that the density difference can be decomposed into fragment differences, one for the surface and another one for the adsorbate: $\Delta\rho(r) = (\rho_{\text{S}}(r) - \rho_{\text{S}}^0(r)) + (\rho_{\text{I}}(r) - \rho_{\text{I}}^0(r))$. It is interesting to see from Fig. 4 that, outside of the bonding region, the density difference is equal to one of those fragment differences, however in the bonding region both components contribute in agreement with the covalent nature of the chemical bond. Since $\Delta\rho(r)$ integrates to zero, in this case, both fragment differences integrate to opposite values, the corresponding charge transfer.

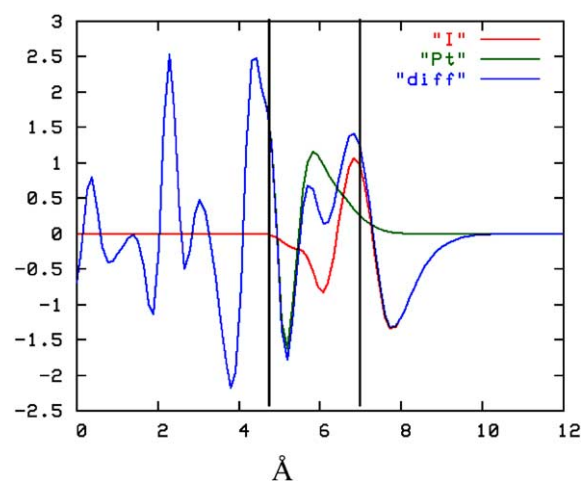


Fig. 4. Iodine Hirshfeld fragment density difference $\rho_{\text{I}}(r) - \rho_{\text{I}}^0(r)$ (I), Pt surface Hirshfeld fragment density difference $\rho_{\text{S}}(r) - \rho_{\text{S}}^0(r)$ (Pt) as obtained for the fcc site in (2×2) cell, and density difference $\Delta\rho(r)$ (diff), averaged over XY plane. X -axis indicates the vertical distance from the third Pt layer. Iodine is positioned at $Z = 6.67$ Å. The bonding region (between the first Pt layer and iodine atom) is indicated by black vertical lines.

Our results indicate qualitative agreement in charge transfer and quantitative agreement in adsorption energies with previous experimental data. Therefore, we believe that our results could contribute to better interpretation of recent experiments in adsorbate-substrate systems at atomic level.

6. Conclusions

The present study uses the plane-wave DFT formalism for the description of iodine adsorption on the Pt(111) surface. We show that this methodology is appropriate for the ab initio analysis of the I–Pt(111) system. The charge transfer and the adsorption energies obtained in this work get along with the trends suggested from experimental studies. This paper proposes the use of the Hirshfeld stockholder partitioning scheme for the analysis of charge transfer in adsorbate-substrate systems and it is successfully applied for the description of our system. The results seem to indicate that this partitioning scheme could be very promising for further studies in surface science and solid state systems. On the other hand, this work suggests that previous finite cluster models are not appropriate for the description of the I–Pt(111) system for the degree of coverage regimes experimentally available up to date [7].

The present approach provides reliable charge transfer effects, adsorption energies and the geometry of iodine adsorbed on different sites of the Pt(111) surface, these data could be of use for detailed interpretation of experimental results and in different theoretical models.

Acknowledgement

Financial support for A.C. and M.G. was provided by CONACYT, México, with the projects 39622-F and 36482-E, respectively. Financial support for N.B. was provided by Instituto Mexicano del Petroleo (IMP), project FIES-98-100-I. A.T. gratefully acknowledges the fellowship from CONACYT, México. We thank the Laboratorio de Supercomputo y Visualización en Paralelo

(LSVP) at UAM-Iztapalapa for the access to its computer facilities. We thank the assistance of Felipe Aparicio for generating the pseudopotentials used in this work.

References

- [1] J.L. Stickney, S.D. Rosasco, G.N. Salaita, A.T. Hubbard, *Langmuir* 1 (1985) 66.
- [2] A.T. Hubbard, *Chem. Rev.* 88 (1988) 633.
- [3] B.C. Schardt, S.L. Yau, F. Rinaldi, *Science* 243 (1989) 1050.
- [4] S.C. Chang, S.L. Yau, B.C. Schardt, M.J. Weaver, *J. Phys. Chem.* 95 (1991) 4787.
- [5] D.G. Frank, O.M.R. Chyan, T. Golden, A.T. Hubbard, *J. Phys. Chem.* 97 (1993) 3829.
- [6] M. Saily, K.A.R. Mitchell, S.A. Furman, M. Labayen, D.A. Harrington, *Surf. Rev. Lett.* 6 (1999) 871.
- [7] O.M. Magnussen, *Chem. Rev.* 102 (2002) 679, and references therein.
- [8] M. Labayen, S.A. Furman, D.A. Harrington, *Surf. Sci.* 525 (2003) 149.
- [9] A. Ignaczak, J.A.N.F. Gomes, *J. Electroanal. Chem.* 420 (1997) 71.
- [10] M.T.M. Koper, R.A. van Santen, *Surf. Sci.* 422 (1999) 118, and references therein.
- [11] F.L. Hirshfeld, *Theo. Chim. Acta* 44 (1977) 129.
- [12] R.F. Nalewajski, R.G. Parr, *Proc. Natl. Acad. Sci. USA* 97 (2000) 8879; R.F. Nalewajski, *Phys. Chem. Chem. Phys.* 4 (2002) 1710.
- [13] F. de Proft, C. Van Alsenoy, A. Peeters, W. Langenaeker, P. Geerlings, *J. Comput. Chem.* 23 (2002) 1198.
- [14] F. de Proft, R. Vivas-Reyes, A. Peeters, C. Van Alsenoy, P. Geerlings, *J. Comput. Chem.* 24 (2003) 463.
- [15] R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- [16] J. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [17] S. Ismail-Beigi, T. Arias, *Comput. Phys. Commun.* 128 (2000) 1.
- [18] N. Trouillier, J.L. Martins, *Phys. Rev. B* 43 (1991) 1993.
- [19] A. Kokalj, M. Causá, *J. Phys. Condens. Matter* 11 (1999) 7463.
- [20] R.W.G. Wyckoff, *Crystal Structures*, second ed., Interscience, New York, 1963.
- [21] R.F.W. Bader, *Atoms in molecules International Series of Manuscripts on Chemistry*, Oxford University Press, Oxford, 1994.
- [22] A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure*, McGraw-Hill, New York, 1982, p. 149.
- [23] K. Horn, M. Scheffler, *Handbook of Surface Science: Electronic Structure*, North-Holland, Elsevier, Amsterdam, 2000.