Bonding of Atomic S to Pt(111) from ab Initio Explicitly Correlated Cluster Model Wave Functions

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The ab initio cluster model approach has been applied to the study of chemisorption of atomic S on Pt(111). Hartree−Fock and explicitly correlated wave functions predict reasonable results for the equilibrium distance perpendicular to the surface and its corresponding vibrational frequency. However, the interaction energy has been shown to be largely affected by electronic correlation effects. Use of MR-MP2 and MRCI wave functions with large reference spaces results in a D_e value which is surprisingly close to the experimental estimate of the interaction energy. All approaches suggest that S is strongly bonded to the Pt(111) surface through covalent interactions but also predict that chemisorbed S exhibits a rather large negative charge. Therefore, it is predicted that S chemisorption will strongly affect the electronic properties of the Pt(111) surface. This situation will be specially valid in the low-coverage limit.

I. Introduction

Platinum's extraordinary catalytic properties make it one of the catalysts that are most commonly employed in industrial processes. These properties are so unique that platinum may be presented as one of the most versatile, all-purpose, heterogeneous metal catalysts.[1] Many of the important practical applications concern chemical processes that are relevant to petroleum refining.[2] A frequent problem encountered in heterogeneous catalysis is that of catalyst poisoning. In the case of platinum catalysts used in oil refining, the presence of sulfur largely affects its catalytic performance.[3] Because of these poisoning properties, the interaction of S with Pt surfaces has been the subject of a considerable attention, especially from the experimental point of view.

The structure of well-ordered S overlayers on Pt(111) has been determined by low energy electron diffraction, LEED, techniques[4] which show S to occupy the fcc sites resulting in a $(\sqrt{3}\times\sqrt{3})R30°$ structure and with a Pt−S bond length of 2.28 ± 0.03 Å. This well-ordered structure is produced at an absolute sulfur coverage of $^1/_3$ ML. For this system, high resolution electron energy loss spectroscopy, HREELS, experiments support the existence of a single type of chemisorbed S as only a single sulfur−platinum stretching vibrational mode appears at 375 cm^{-1}.[5,6] Recent photoemission and thermal desorption spectroscopy, TDS, studies suggest that other high-symmetry surface sites, hcp or bridge, may also be occupied at coverages higher than 0.3 ML.[7]

In order to understand the origin of the sulfur poisoning effect, some effort has been devoted to clarify the chemical nature of the interaction of the interaction between sulfur and single-crystal Pt surfaces.[8−10] These studies indicate that changes on the reactivity of the Pt surface originated by sulfur chemisorption are due to electronic effects. This is contrary to previous work based on the changes of work function of Pt(111) with sulfur coverage.[11] In fact, the work function measurements have been interpreted in terms of a strong covalent bond between sulfur and the metal substrate, and the authors conclude that chemisorbed sulfur presents some positive charge.[11] This picture connotes that sulfur chemisorption does not direct important electronic effects. However, this description is in clear contradiction with chemical intuition. In fact, for a rather electronegative adatom such as sulfur on a metal surface, one would expect the net charge on sulfur be at least negative. Recent qualitative molecular orbital calculations do in fact predict a modest negative charge on sulfur.[7]

The nature of the chemical bond between an adsorbate can be well-described by means of the ab initio cluster model approach.[12−16] This theoretical approach permits a detailed analysis of the surface chemical bond, and depending on the quality of the ab initio wave function, it permits a rather quantitative description of several properties.[17−19] The application of this method to platinum surfaces has been, however, quite limited because of the difficulty to treat large clusters of platinum atoms. To circumvent this problem a one-electron pseudopotential was developed by Zurita et al.[20] With the help of this pseudopotential and of a mixed pseudopotential approach it has been possible to study the electron structure of Pt clusters[21] and to describe the electrostatic potential maps of Pt surfaces[22] and some adsorbate−Pt surface interactions such as CO/Pt(111)[23] or O/Pt(111).[24,25]

In this work we will apply the ab initio cluster model approach to the low-coverage limit of the S/Pt(111) system. In particular we will show that the present theoretical approach permits a rather accurate description of structural parameters such as equilibrium geometry, vibrational frequency, and bonding energy. This reliable description of the interaction will permit us to exact information about the nature of the S−Pt(111) chemical bond. This will be accomplished by making use of well-established theoretical methods of analysis of the wave function[12,16] and, also, of the recently proposed charge distribution analysis, CDA, method.[26]

This paper is organized as follows. Section II briefly describes the cluster models used to describe the Pt(111) surface. Next, in section III, we disclose some computational details and a short description of the theoretical methods of analysis. Calculated structural parameters are discussed in section IV

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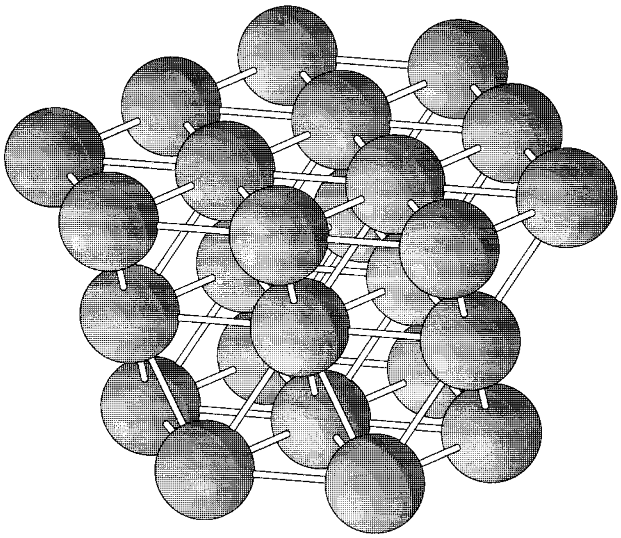

Figure 1. Schematic represenation of the Pt_{25} cluster model used to represent the Pt(111) surface.

whereas analysis of the interaction will be reported in section V. Finally, we present our conclusions in section VI.

II. Surface Cluster Models

In this work we represent the Pt(111) surface by means of a moderately large cluster model. For this surface cluster cluster we define a "local" region and an "outer" region. The local region consists of the substrate atoms which are directly involved in the bonding with sulfur, and the remaining cluster atoms define the "outer" region whose role is to provide an adequate coordination and embedding to the local region. This partition is in spirit similar to the embedding technique employed by Whitten et al.,[27] although we will not make use of any localization procedure nor will we discard any set of orbitals to account for electronic correlation effects. The cluster model partition permits a better description of the "local" region while retaining a reasonable description of the "outer" part of the model and thus permits the ab initio treatment of the large cluster models used in this work.

In this work we concentrate our study of the S chemisorbed at the fcc site of Pt(111) which is represented by a Pt_{25} cluster model (FIgure 1). This cluster is made of three layers and having 12 atoms in the first, 7 in the second, and 6 in the third layer; this is indicated as $Pt_{25}(12,6,7)$. This cluster model belongs to the C_{3v} symmetry point group and the the C_3 axis passes through the fcc active site.

III. Computational Details

The electronic structure of the Pt_{25} and $Pt_{25}-S$ clusters defined above has been studied by means of ab initio techniques. Hartree–Fock, self consistent field, SCF, wave functions and, also, more sophisticated calculations with extensive inclusion of electron correlation effects were carried out for the interaction of sulfur about the fcc site.

The basis sets and pseudopotentials used in this work are as follows. The Pt atoms belonging to the "local" region are described with a relativistic pseudopotential that leaves explicitly the $5d^{10}$ electrons on the valence shell. For these atoms the Gaussian-type orbital, GTO, basis set is (6s4p6d/3s2p3d). The Pt atoms defining the "outer" region are treated with the help of a recently derived one-electron pseudopotential which contains a core with a spherically averaged d^9 shell. Two different GTO sets have been used for these "environmental" Pt atoms. The SCF calculations were done using either a (4s3p/2s1p) basis set (basis 1) or a (4s/2s) set (basis 2) whereas explicitly correlated calculations were carried out using basic 2 only (see refs 20−23). Finally, we include all electrons of the S atom and have chosen a (13s9p1d/6s4p1d) basis set taken from ref 28. Further details and additional information about the Pt pseudopotentials has been reported elsewhere.[23−25]

Because of the particular way in which the surface cluster models were chosen they contain always an even number of electrons leading to a closed shell singlet state. We must advert that many electronic states exist in a very narrow interval of energy (≈0.2 eV). This is characteristic of the bulk metals and is a good indication about the ability of the cluster models to represent the metallic character of the substrate. Adding $S(^3P)$ to the Pt_{25} surface cluster model results in a $^3A_2$ state for the $Pt_{25}-S$ supersystem arising from an e^2 open shell occupation. Here too, different electronic states appear in narrow energy interval.

For our cluster model representing the Pt(111) fcc site, electronic correlation effects were introduced through a variety of theoretical techniques. This includes single and multireference second-order perturbation methods. SR-MP2 and MR-MP2, and selected multireference configuration interaction, MRCI. For the SR- and MR-MP2, we use the barycentric Møller–Plesset partition as in the CIPSI algorithm.[29−33] For MR-MP2 the reference space was iteratively constructed so as to include all determinants contributing to the perturbed first-order wave function by a first selection threshold $\tau_R = 0.1$ or 1% in the variational reference space. The MRCI calculations start from the MR-MP2 reference space but determinants with a contribution to the first-order wave function larger than a second-selection threshold, $\tau_V = 0.002$, are treated variationally. The reference space constructed with $\tau_R = 0.1$ contains only the 5 most important determinants, which are taken as references from which single and double excitations generated about 46×10^6 determinants. For this set of generated determinants $\approx 3 \times 10^4$ are included in the variational expansion. Using the selection thresholds described above, potential energy curves were obtained and the MR-MP2 and MRCI interaction energies were later refined by using lower selection thresholds until the final value was reasonably converged. For the MR-MP2 we used selection thresholds of $\tau_R = 0.1$, 0.04, and 0.02, resulting in reference spaces of 5, 46, and 260 reference determinants, respectively. For each value of τ_R two different thresholds, $\tau_V = 0.002$ and 0.001, were used to select the variational space included in the MRCI wave functions. As expected from the structure of the CI problem, the dimension of the variational space is very sensitive to τ_V, and small changes in this value lead to considerable changes in the final dimension of the CI space. The variational spaces thus constructed vary from $\approx 3 \times 10^4$ to $\approx 10^5$, and the variational CI accounts for more than 50% of the total electronic correlation. The calculation with $\tau_R = 0.02$ involves the generation of about 10^{10} determinants whose contribution to the energy up to second order is explicitly calculated. However, the MR-MP2 interaction energy computed with this tremendous second-order expansions only differ by about 0.3 eV (or 7%) with respect to the one obtained with $\tau_R = 0.04$. The convergence of the MRCI expansion is even better: the calculation with $\tau_R = 0.04$ and $\tau_V = 0.001$ does only differ by 0.15 eV from the one obtained using $\tau_R = 0.02$ and $\tau_V = 0.001$, although the computation time for the later is about 5 times larger than for the former. The use of different thresholds for the reference and variational spaces enabled us to investigate the convergence of the CI wave function and to put error bars in the calculated MR-MP2 and MRCI results. Therefore, the calculated values for the correlated interaction energies can be considered to be accurate to approximately ±0.1 eV.

In addition to the problem of having a reasonably well-converged value for the correlated interaction energy, it is necessary to realize that the use of finite basis sets bears the unavoidable basis set superposition error, BSSE. To avoid possible computational artifacts and to be able to predict an accurate value for the chemisorption bond interaction energies, it is necessary to investigate the extent of BSSE and, if possible, to correct it. The SCF interaction energies have been corrected by using the standard Boys−Bernardi counterpoise method.[34] For MR-MP2 and MR-CI we used a slightly procedure. Here, the basis superposition to the total energy was calculated by using the procedure described in the recent work of Yang et al.[35−37] Therefore, the BSSE was estimated by calculating the energy of the Pt cluster with the S virtual basis present (but not the S nucleus). For the system studied in the present work and within the basis sets above described the BSSE at the SCF level is less than 0.1 eV and it is of ≈0.25 eV at both the MR-MP2 and MRCI levels. This is in the range described by Yang et al. for several adsorbates on Ni(111). Considering that the present calculations deal with a cluster model containing 26 atoms, 25 Pt cluster atoms plus the S adsorbate, the BSSE contributions are not exceedingly large. In fact, it is a small fraction of the total interaction energy (vide infra).

All calculations have been carried out using a locally modified version of the HONDO-CIPSI suite of programs.[38]

IV. Structural Parameters for the S/Pt(111) System

In this section we report the structural parameters that can be obtained for the perpendicular motion of atomic S above the fcc site. Potential energy curves have been obtained at all levels of theory described in the previous section. For each theoretical method the potential energy curve has been fitted to a third-degree polynomial. From this fit the equilibrium distance perpendicular to the surface, z_e, and the vibrational frequency for the normal mode perpendicular to the surface, ν_e, have been obtained. The SCF and SR-MP2 interaction energy, D_e, is obtained by subtracting the energy of the fragments from the energy at the minimum of the potential energy curve. For for the MR-MP2 and MRCI D_e is computed by subtracting from the energy at the minimum of the potential energy curve that results from a calculation performed at infinite (i.e., 10^6 au) separation. This later approach has been used as a way to minimize non-size-consistent effects derived from the truncated CI inherent to the methods. Also, the use of a supermolecule approach to compute the energy of the separate systems minimizes possible artifacts due to the use of a selected MRCI.[39] To take away the BSSE, all D_e values have been corrected as indicated in the previous section.

First, we will discuss the dependence of calculated results on the basis set used to describe the cluster "outer" region. The only difference between both basis sets in the inclusion of 6p functions in the Pt one-electron environmental pseudoatoms. From the summary of results reported in Table 1 we see that as far as Hartree−Fock properties are concerned there are not large variations between both sets of results. The values for z_e and ν_e are almost identical, and the BSSE-corrected D_e values differ by ≈0.1 eV. Therefore, the descriptions of both basis sets are close enough so as to be able to use basis 2 in the correlated calculations. This argument is reinforced by the results of the Mulliken population analysis; both basis sets predict that S is negatively charged by ≈−0.3e. Even more indicative than the Mulliken net charges are the magnitude of the dipole moment, μ, and of dipole moment first derivative $(d\mu/dz)_{z_e}$ reported in Table 1. The dipole moment and, more specifically, its first derivative provides an excellent measure of the charge on the adsorbate (see, for instance refs 40 and 41). The fact that both values are similar indicate that both basis sets describe the same "chemistry". Moreover, the large curvature of the dipole moment curve indicates that, in both cases, the bond is not ionic. In the next section we will further discuss these quantities and compare them with those resulting from MRCI wave functions.

TABLE 1: Hartree−Fock Results for Different Structural Parameters Corresponding to the Interaction of Atomic S above the fcc Site of Pt(111) As Represented by a Pt_{25} Cluster Model[a]

property	basis 1	basis 2
z_e (Å)	1.84	1.83
ν_e (cm^{-1})	311	319
D_e (eV)	0.90	1.03
Q_S	−0.30	−0.35
μ (au)	−0.958	−0.923
$(d\mu/dz)_{z_e}$	−1.031	−0.733
$^1/_2(d^2\mu/dz^2)_{z_e}$	+0.439	+1.134

[a] Reported are the equilibrium distance, z_e, vibrational energy, ν_e, BSSE-corrected interaction energy, D_e, Mulliken charge, Q_S, dipole moment, μ, and dipole moment derivatives, $(d\mu/dz)_{z_e}$ and $^1/_2(d^2\mu/dz^2)_{z_e}$. Basis 1 and basis 2 are (4s1p/2s1p) and (4s/2p), respectively, for the "outer" region atoms.

TABLE 2: Explicitly Correlated Results for Different Structural Parameters Corresponding to the Interaction of Atomic S above the fcc Site of Pt(111) As Represented by a Pt_{25} Cluster Model[a]

method	z_e (Å)	ν_e (cm^{-1})	D_e (eV)
SR-MP2	1.88	424	4.98
MR-MP2	1.88	420	4.01
MRCI	1.80	330	4.09
expt	1.62[4]	375[5,6]	3.93[42,43]

[a] Symbols are as in Table 1; methods are as defined in section III.

Having established that basis 2 is adequate enough to describe the S−Pt interaction we turn now our attention to the results which explicitly include electronic correlation effects and compare with the available experimental data. As explained in the Introduction, reliable experimental measurements exist for z_e and ν_e through quantitative LEED[4] and HREELS[5,6] measurements. To the author's best knowledge there is no direct measurement of the interaction energy of atomic S and Pt(111). A rough estimate can be obtained from the thermodynamic data reported by Benard et al.[42] and the experimental dissociation energy of the diatomic S_2 molecule.[43] Simple calculations lead a estimate of 3.93 eV for the experimental value of the interaction energy, D_e, of S with the Pt(111) surface. However, we must point out that this value cannot be taken as a precise and direct measure of the chemisorption energy. A precise value can be obtained by using microcalorimetric techniques. Unfortunately such measurements for S on Pt(111) have not been carried out yet.

A summary of results including electronic correlation effects is collected in Table 2. First, let us comment of the second-order results. Both, SR-MP2 and MR-MP2 lead to similar results for the equilibrium distance and vibrational frequency which are increased with respect to the SCF values contrarily to what is expected. However, the SR-MP2 calculated D_e value, corrected by BSSE, is too large and reflects the well-known fact that second-order overestimates the electronic correlation effects.[44] In fact, the MR-MP2 values are similar to the MRCI ones, and they provide a reasonable estimate of D_e and represent substantial improvement with respect to the SCF ones. The fact that MR-MP2 and MRCI are so close is a new indication of the importance of higher-order effects at the MR-MP2 and which are already introduced through the quadruple excitations generated from the double excitations included in the reference space. The final calculated value of ≈4.0 eV is in very good agreement with the "experimental" value. Given the limitation of the cluster model and basis set used and the way the experimental value has been obtained, the agreement between both quantities may be excessively good. However, the important points are that the order of magnitude is the same and that S is predicted to form a strong bond with Pt(111). Moreover, this strong bond has a very large contribution from electronic correlation effects. This is similar to the situation previously found for O on Pt(111). However, there is an important qualitative difference between O and S. The first is predicted to be unbound at the Hartree−Fock, SCF, level whereas a net bond of ≈1 eV is found for S. The origin of this difference will be further discussed in the next section.

V. Analysis of the Bonding of S to Pt(111)

In principle, the important contribution of electronic correlation to the bonding interaction between atomic S and the PT$_{25}$ cluster model seems to indicate that the analysis of the interaction should be done based on an extensively correlated wave function only. However, one must realize that the SCF Slater determinant, $|\phi_{\mathrm{SCF}}\rangle$, makes a very important contribution to the MRCI, $|\psi_{\mathrm{MRCI}}\rangle$, wave function. This contribution can be quantified by simply computing the projection of $|\phi_{\mathrm{SCF}}\rangle$ on the $|\psi_{\mathrm{MRCI}}\rangle$, which is simply given by the $\langle\phi_{\mathrm{SCF}}|\psi_{\mathrm{MRCI}}\rangle$ integral. In the present case we find $\langle\phi_{\mathrm{SCF}}|\psi_{\mathrm{MRCI}}\rangle \approx 0.9$, indicating that $|\phi_{\mathrm{SCF}}\rangle$ is responsible for roughly 80% of $|\psi_{\mathrm{MRCI}}\rangle$. This contribution is much larger than the one recently reported for O on Pt(111) where $\langle\phi_{\mathrm{SCF}}|\psi_{\mathrm{MRCI}}\rangle \approx 0.8$, indicating that $|\phi_{\mathrm{SCF}}\rangle$ gives only 64% of the MRCI wave function.[25,45]

Before carrying out a detailed analysis of the interaction we would like to briefly comment on the net charges on the adsorbate which are predicted by means of the Mulliken population analysis. Both basis sets, basis 1 and basis 2, result in a net charge on chemisorbed S which is of ≈−0.3e only. This is not consistent with the large slope of the dipole moment curve that are obtained at the SCF level. Even assuming that the Hartree−Fock wave function tends to overestimate the ionic character of the wave function, we must recall that both estimates of the net charge on the adsorbate, Mulliken charges and dipole moment curves, are obtained from the same Hartree−Fock wave function. The Mulliken charges are in fact too small. This is not at all surprising,[46] and it is the reason why the analysis of the chemisorption bond based on dipole moment curves was proposed as an alternative to the Mulliken population analysis.[40,41]

In order to further analyze the bonding interaction, we have computed the dipole moment curve at the SCF and MRCI levels. The SCF and MRCI dipole moment curves exhibit a similar shape indicating that the two descriptions of the bond cannot be very different (Figure 2). Information about the nature of the bond can be obtained from the dipole moment curve assuming a Taylor series development of the dipole moment near the equilibrium position. As discussed elsewhere,[40,41] the slope of the dipole moment curve for the motion of an adsorbate perpendicular to the surface is related to the net charge on the adsorbate. The dipole moment and the first and second derivative are reported on Table 3 for the SCF and MRCI wave functions. Interestingly enough the SCF and MRCI values for the slope of the dipole moment curve are almost identical, suggesting that the net charge on S is about −0.7e, independent of the wave function used. Notice that this is twice the value which is predicted by the standard Mulliken population analysis. Again, this is different from previous results for O above the fcc site of a Pt(111) surface cluster model where the dipole first derivative is reduced from −1.25 to −0.94.

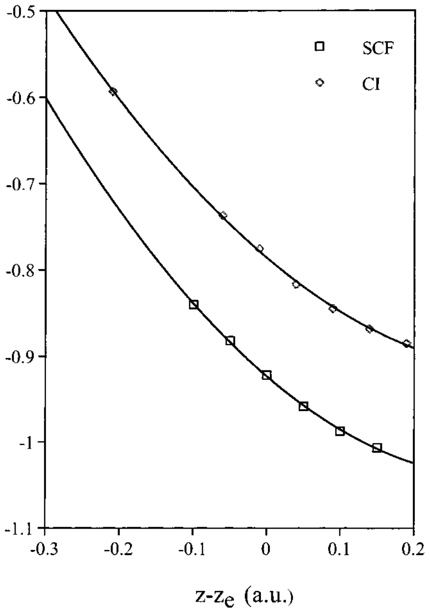

Figure 2. Dipole moment curves for the interaction energy of S above the fcc site of the Pt$_{25}$ cluster model, obtained from ab initio SCF and MRCI wave functions.

TABLE 3: SCF and MRCI Dipole Moment and Dipole Moment Derivatives, μ, $(d\mu/dz)_{z_e}$, and $^1/_2(d^2\mu/dz^2)_{z_e}$, Respectively[a]

property	SCF	MRCI
μ	−0.923	−0.788
$(d\mu/dz)_{z_e}$	−0.733	−0.723
$^1/_2(d^2\mu/dz^2)_{z_e}$	+1.134	+1.004

[a] All results in atomic units.

The calculated value for $(d\mu/dz)_{z_e}$ cannot be taken as a direct measure of the net charge because the metal surface polarizes and, as a consequence, the dipole moment derivative is usually smaller than the net charge in the atom. To avoid the effect of the surface polarization, Bagus et al.[26] have recently proposed to obtain the net charge from the slope of the dipole moment curve computed with the molecular orbitals corresponding to the equilibrium distance and keeping them frozen. In this way undesired effects arising from substrate polarization are avoided and the charge on the adatom is directly defined by the adsorbate basis functions. This analysis, termed charge distribution analysis, CDA, after Bagus et al.[26] provides a simple method to estimate net charges which does not rely in arbitrary partitions of the electron density as in the Mulliken analysis nor does it imply costly numerical integration as in other methods currently used in quantum chemistry. The CDA is carried out using the SCF density and predicts a net charge on S of −0.81 ± 0.05, with the error bars obtained from CDA calculations for S moving parallel or perpendicular to the surface and using either basis 1 or basis 2.

The CDA analysis is consistent with that of the dipole moment curves and indicates a largely negative-charged S adatom. However, the large curvature of the dipole moment curve indicates that the bond cannot be regarded as purely ionic. Further information about the nature of the chemisorption bond can be obtained from the constrained space orbital variations, CSOV, technique.[47−49] The CSOV analysis permits the decompostion of the interaction energy in intraunit (or polarization) and interunit (or charge-transfer covalent) contributions. As usual, we start by constructing a frozen orbital wave function, $|\psi_{FO}\rangle$, by superimposing the electron densities, or molecular orbitals, of Pt_{25} and S. At this step the interaction is repulsive by 4.8 eV. This original Pauli repulsion is lowered by inter- and intraunit bonding contributions. Usually after the first CSOV cycle the SCF energy is almost completely recovered. Here, however, after allowing adsorbate and substrate to polarize and to donate charge in both directions to form covalent bonds the interaction is still repulsive by $\approx$2.5 eV, and a second CSOV cycle is necessary to achieve the SCF D_e value. This is a clear indication of the formation of a strong covalent bond. The change in energy at each CSOV step is accompanied by changes in the variational wave function. These changes can be measured by the overlap integral between $|\psi_{FO}\rangle$ and the variational wave function. After the first CSOV cycle this overlap is 0.91, but it decreases to 0.32 for the final SCF wave function! This is a clear indication that the final wave function contains a strong mixing of the molecular orbitals of the two units. The final SCF wave function barely resembles the one constructed by superimposing the wave functions of the constituent units. However, the resulting wave function is strongly polarized towards the sulfur atom.

Finally, we would like to comment on the physical nature of the electron correlation effects. The comparison of the $\langle\phi_{SCF}|\psi_{MRCI}\rangle$ values for O and S on Pt(111) is consistent with a more pronounced effect of correlation in chemisorbed O where the MRCI value for the slope of the dipole moment curve also indicates that electronic correlation results in an enhancement of covalent effects. Still, it is difficult to understand why electronic correlation makes such an important contribution to the interaction energy. When the bond is largely ionic, the importance of electronic correlation is consistent with the poor description of adsorbate electron affinity and cluster model ionization potential, which is a measure of the surface work function.[41,50] However, this is not the case for either O or S on Pt(111) where strong covalent effects are present. A possible explanation comes from the comparison between Pauli repulsion between either O or S and the Pt_{25} cluster which is of 7.3 and 4.8 eV, respectively. The larger repulsion found for O is consistent with the shorter distance to the surface and the fact that Pauli repulsion increases exponentially with this distance. The difference in Pauli repulsion is enough to explain the difference between the calculated interaction energy between O or S and the surface cluster model. This suggests that the electronic correlation is precisely the leading physical mechanism to decrease this large initial repulsion. The mixing of the ground state configuration with other determinants where electrons are placed on the more diffuse virtual orbitals will lead to an instantaneous situation where Pauli repulsion is lower. This explanation is also consistent with results reported by Bauschlicher for Co on Cu_n clusters representing the Cu(100) surfaces.[51] Bauschlicher has shown that the oscillations on the SCF D_e which arise from the different Pauli repulsion effects in different clusters[52] are removed by explicit inclusion of electronic correlation effects. The present interpretation for the physical nature of electronic correlation effects holds for CO on Cu(100) and for either O or S on Pt(111).

VI. Conclusions

The ab initio cluster model approach has been applied to the study of chemisorption of atomic S on Pt(111). Hartree−Fock and explicitly correlated wave functions lead to reasonable results for the equilibrium distance perpendicular to the surface and its corresponding vibrational frequency. However, the interaction energy has been shown to be largely affected by electronic correlation effects. At the Hartree−Fock level, S is predicted to be already bonded to Pt(111), but the interaction energy is only 25% of the value estimated from experimental data. On the other hand, the D_e values obtained through SR-MP2 are close to the experimental estimated values but overestimate the strength of the interaction. Use of MR-MP2 techniques or of MRCI wave functions, with large reference spaces, results in values which are surprisingly close to the experimental estimate of the interaction energy. The coincidence between MR-MP2, MRCI, and experimentally derived D_e may be fortuitous, but both MR-MP2 and MRCI results clearly show the importance of higher-order effects.

In spite of the tremendous influence of electronic correlation to the interaction energy, the picture of the chemisorption bond emerging from both SCF and MRCI wave functions is very similar. This is logical since the SCF contains about 80% of the total wave function, a contribution which is rather large compared to that recently reported for O on Pt(111). Both SCF and MRCI approaches denote that S is strongly bonded to the Pt(111) surface through covalent interactions. This is in agreement with the behavior of S as a metal ligand. However, both approaches also predict that a rather large negative charge exists on chemisorbed S. This is consistent with the very recent experimental studies of S on Pt(111) electrodes of Sun et al.[53] Moreover, these authors suggest that the negative charge on chemisorbed S plays an important role in controlling hydrogen adsorption and, therefore, the surface catalytic properties. The present results are in good agreement with these findings and insinuate that chemisorption of S involves strong electronic modifications of the surface. One last point concerns the interpretation of the experiments involving changes on the Pt(111) work function upon S chemisorption. The usual interpretation of these experiments implies that the adsorbate is not charged or has a small positive charge. However, we must advert that this usual interpretation is not correct because it neglects important effects such as the surface polarization in response to the adsorbate charge.[54] Finally, comparison with a previous study involving chemisorption of O on Pt(111) manifests that the importance of electronic correlation in the calculated D_e is largely related to the Pauli repulsion between the adsorbate and the surface. The configuration interaction mixing permits the inclusion of instantaneous situations in which two or more electrons occupy more diffuse virtual orbitals, thus lowering the initial Pauli repulsion.

In summary, sophisticated ab initio calculations predict that S binds to Pt(111) with a strong-covalent bond but with a considerably large negative charge in the chemisorbed S. Therefore, S chemisorption will strongly affect the electronic properties of the Pt(111) surface. This situation will be especially valid in the low-coverage limit.

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