Inelastic electron tunneling spectroscopy (IETS) performed with the scanning tunneling microscope (STM) has given us unprecedented insight into the chemical structure of matter on the atomic scale [1–3]. In this respect, state-of-the-art theoretical simulations, which use the electronic structure calculated with local or semilocal density functional theory (DFT) as the initial ingredient, have proven to be essential to interpret the recorded STM [4] and the IETS signals [5–7]. Still, there is an emblematic experiment for which most sophisticated IETS simulations have failed: the conductance decreases observed over the vibrational thresholds of O$_2$ on Ag(110) [8]. More precisely, STM-IETS gives signals for only one of the chemisorption states, the one with the molecular axis along the [001] surface direction (henceforth, O$_2$[001]).

In general, the IETS signal corresponds to an increase of the STM conductance because the excitation of a vibrational mode opens an additional channel for conduction [5,9–11]. Nevertheless, when a molecular state is resonant with the Fermi energy ($E_F$), virtual vibrational excitations are important, and a decrease in conductance is predicted [9,10]. To date, the O$_2$[001] is the only case for which conductance decreases have been reported. However, the simulated IETS of O$_2$[001] have consistently produced decreases of conductance instead of the experimental decreases [7,10]. Given that the DFT electronic structure predicts $\pi$-$\pi^*$ resonances away from $E_F$ [see Fig. 1(a)], the published conclusions were that the $\pi$-$\pi^*$ resonances were wrongly positioned with respect to the Fermi level [7,10]. Nevertheless, questioning the position of the Fermi level and, thus, the molecular charge state in this system is at variance with the excellent characterization of the two experimental chemisorption states given by this theory [12], the O$_2$[001], and the one with the molecular axis along the [110] direction (O$_2$[110]). Moreover, the Fermi level fitting cannot reproduce the rich IETS structure of the experimental data showing increases and decreases according to the vibrational mode and the tip localization.

In this Letter, we present DFT calculations corrected by static correlations (DFT + $U$) [13] in combination with STM-IETS simulations [5,7]. We find that the chemisorbed O$_2$ retains a finite spin moment only in one of the two possible chemisorption geometries, namely, the O$_2$[001]. The origin of this paramagnetic state is a molecular orbital pinned at the Fermi level, giving rise to a molecular mixed-valent state [14]. The corresponding electronic structure leads to IETS simulations where the experimental change in conductance and also their spatial tip-position dependence are explained giving unprecedented information on the electronic and vibrational symmetries at work.

Density functional theory calculations are performed with the VASP code using plane waves with an energy cutoff

![FIG. 1 (color online). Spin-up (positive) and spin-down (negative) projected density of states of O$_2$/Ag(110) onto the O$_2$ molecular orbitals. The molecule is chemisorbed along the [001] direction. (a) Semilocal DFT (GGA) results. (b) Semilocal DFT + $U$ results ($U = 3$ eV). Intra-atomic correlation leads to a change in the $\pi^*$ resonance by splitting its spin components following a Stoner-like process. The Gaussian broadening used in the projection is 0.25 eV.](image-url)
of 515 eV and the projector augmented wave method (PAW) [15]. We use a periodic supercell consisting of a six-layer slab separated by 10.45 Å of vacuum and a large (3 × 4) surface unit cell in order to approach the dilute overlayer limit. The surface Brillouin zone is sampled with a 4 × 4 × 1 Monkhorst-Pack grid of special k points. The exchange and correlation energy is calculated within the generalized gradient approximation (GGA) using the Perdew and Wang functional (PW91) [16]. Vibrational modes are then obtained from the diagonalization of the dynamical matrix, which is calculated by a finite-difference method implemented in VASP. The IETS simulations are performed using the many-body extension of the Tersoff-Hamman approximation for the STM [5,7].

The inclusion of static correlations via the DFT + U treatment does not impoverish the excellent GGA description of the adsorption molecular properties. Indeed, the DFT + U method is known to correct the electronic spectrum without perturbing the physical magnitudes for which the standard DFT excels. A detailed comparison of these quantities is shown in Table I. Corrections to the screened on-site Coulomb repulsion are applied to the oxygen 2p electrons [17] following the rotationally invariant DFT + U scheme proposed by Dudarev et al. [18]. The electronic structure giving rise to the mixed-valent regime, Fig. 1(b), is obtained for 2 eV ≤ U ≤ 4 eV. The computed U is about 4 eV using the constrained DFT of Cococcioni and Gironcoli [19] to evaluate the energy cost of adding extra charge to O2 when adsorbed on Ag(110). The U value depends on the actual projectors and the constraining method used to fix the orbital occupation. However, we have verified that such limitation does not affect the final electronic structure in the present case.

The molecular electronic structure is subject to a Stoner-like process for the chemisorbed O2[001], but not for the O2[110]. The large screening of the molecule chemisorbed along the [110] direction quenches its intrinsic magnetism. Along the [001] axis, the molecule is more distant from the surface leading to a reduced screening and a stronger molecular character. This is seen in Fig. 1. There, the density of states (DOS) is plotted according to its molecular character by projecting it onto the O2 molecular orbitals (MO). As seen in Fig. 1(b), there is a Stoner-like splitting of the highest occupied MO due to the intramolecular U. The spin splitting of this orbital, the perpendicular-to-the-

<table>
<thead>
<tr>
<th>O–O (Å)</th>
<th>O–Ag (Å)</th>
<th>O2-surface (Å)</th>
<th>O2-induced charge (Bader analysis in e)</th>
<th>magnetization (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>1.43</td>
<td>2.35</td>
<td>1.34</td>
<td>0.95</td>
</tr>
<tr>
<td>GGA + U = 2 eV</td>
<td>1.42</td>
<td>2.36</td>
<td>1.34</td>
<td>0.93</td>
</tr>
<tr>
<td>GGA + U = 3 eV</td>
<td>1.41</td>
<td>2.37</td>
<td>1.34</td>
<td>0.88</td>
</tr>
<tr>
<td>GGA + U = 4 eV</td>
<td>1.39</td>
<td>2.39</td>
<td>1.34</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The spin-polarized DFT + U (GGA + U) quantities describing the physical properties of O2 chemisorbed on Ag(110) along the [001] direction.

The main difference between them despite their sign is that the inelastic contribution involves all possible intermediate electronic states, while the states contributing to the elastic
channel are restricted to an energy interval of the order of the mode frequency \(\hbar \Omega\) about the Fermi energy \([5]\). The topography of the conductance change observed on the \(O_2\) is determined by all the electronic states coupling with the \(\sigma_g\) orbital, which is the state at \(E_F\) controlling the electronic transport process [see Fig. 1(b)]. The symmetry analysis summarized in the table of Fig. 3(e) provides a preliminary idea of the states that couple with the \(\sigma_g\) for each vibrational mode. In case of having various symmetry-allowed couplings, the IETS image is mainly formed by those orbitals with a larger DOS around \(E_F\) \([23]\).

The symmetry characters are analyzed with respect to two elements of symmetry of the system’s point group, namely, reflection by the perpendicular-to-the-surface planes containing the molecular axis \(\sigma_{h'}\) and perpendicular to the molecular axis \(\sigma_v\).

Figures 3(a) and 3(b) are the inelastic and elastic contributions to the stretch mode, respectively. As written in Fig. 3(e), the \(\pi^+\) is antisymmetric (\(A\)) with respect to \(\sigma_v\) and symmetric (\(S\)) with respect to \(\sigma_{h'}\). Since the stretch mode is symmetric with respect to both elements, forcedly the symmetry character of the coupling electronic states has to be \(A\) and \(S\), respectively. This corresponds to the \(\pi^+\) and \(3\sigma_g\) orbitals. The \(\pi^+\) character dominates the DOS at \(E_F\); and, as a consequence, both the inelastic and elastic components in Figs. 3(a) and 3(b) mostly reflect this symmetry. As the elastic correction is much larger than the inelastic one, the excitation of the stretch mode leads to a reduction in conduction except between the O atoms where the \(\pi_g\) orbital presents a nodal plane.
The antisymmetric O$_2$–Ag stretch mode is more complex. The symmetry analysis of Fig. 3(e) shows that the $\pi^\perp_g$ can couple with the $3\sigma_g$ and the perpendicular-to-the-surface $\pi_u$ orbitals, whose DOS about $E_F$ are small [see Fig. 1(b)]. Thus, for equivalent coupling strengths, we would expect a smaller conductance change for the antisymmetric O$_2$–Ag stretch mode than for the O–O stretch mode, as is the case. Figure 3(d) shows that the elastic contribution, which is restricted to states around $E_F$, contains a nodal plane between the O atoms and corresponds to the $\pi^\perp_g$ orbital, which dominates the DOS at $E_F$. In contrast, the summation over all possible intermediate states leads to both the $3\sigma_g$ and the $\pi^\perp_u$ characters of the inelastic contribution, as seen in Fig. 3(e). Summing both contributions, we obtain that the total conductance change is positive in between the two oxygen atoms, where the elastic contribution is zero and the inelastic one is maximal, and negative in the region where the elastic part is maximal and the inelastic part minimal. This result shows the multilevel character of the inelastic process. In order to understand the IETS data, one needs to go beyond single-level models [9]. Yet, our analysis shows the overwhelming importance of having the spin-polarized $\pi^\perp_g$ orbital at the Fermi energy as a key ingredient in the O$_2$/Ag(110) IETS.

This particular electronic structure, with a spin-polarized molecular orbital at the Fermi energy, is also responsible for the mixed-valent character of the chemisorbed O$_2[001]$. Spin polarization naturally appears when the intramolecular correlation $U$ is larger than the resonance width $\Gamma$. Typically, $U$ is inversely proportional to the size of the molecular orbital. Hence, small and weakly adsorbed molecules presenting negative IETS are prone to be in a mixed-valency regime, as demonstrated for the O$_2[001]$. To summarize, we have applied the DFT + $U$ method to adsorbed O$_2$ on Ag(110), and have reproduced the experimental IETS data by Hahn et al. [8]. In doing so, the chemisorption state O$_2[001]$ is characterized as a mixed-valent state, where a spin-polarized molecular orbital dominates the electronic structure at the Fermi energy. Our calculations show that IETS can reveal important information about the electronic structure and magnetic nature of chemisorbed molecules. Thus, IETS arises as a promising tool to characterize the otherwise elusive molecular mixed-valency regime. In this regime, electron correlations are responsible of large charge fluctuations leading to nonadiabatic effects [24]. In this respect, our findings are relevant to explain recent experimental results [25] where O$_2$ can be dissociated with controlled STM pulses when adsorbed in the [110] geometry but not in the [001] one. We suggest that while the O$_2[001]$ is a mixed-valency system, with strong many-body correlations that imply fast vibrational damping, the O$_2[110]$ is not subjected to correlations and its vibrational damping is qualitatively smaller allowing dissociation.

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[17] For checking purposes, we perform DFT + $U$ calculations using the SIESTA code to apply on-site Coulomb corrections to the O$_2$ $\pi_e$ electrons. There are no significant differences in the electronic structure when $U$ is applied to either the atomic 2$p$ or the molecular $\pi_e$ electrons.
[20] The magnitude measured in the experiments is the second derivative of the tunneling current with respect to the sample bias. From these data, the conductance change over the vibrational threshold is then calculated by measuring the area of the peaks in the second derivative.
[23] The weight of the couplings in $\Delta\sigma_{\text{ad}}/\sigma$ is inversely proportional to the energy difference between the $\pi^\perp_g$ and the other coupling orbital [6]. Since the $\pi^\perp_g$ orbital is at resonance with $E_F$, the contribution of the coupling orbitals with larger DOS at $E_F$ is favored.