Kondo conductance across the smallest spin $1/2$ radical molecule

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Molecular contacts are generally poorly conducting because their energy levels tend to lie far from the Fermi energy of the metal contact, necessitating undesirably large gate and bias voltages in molecular electronics applications. Molecular radicals are an exception because their partly filled orbitals undergo Kondo screening, opening the way to electron passage even at zero bias. Whereas that phenomenon has been experimentally demonstrated for several complex organic radicals, quantitative theoretical predictions have not been attempted so far. It is therefore an open question whether and to what extent an ab initio-based theory is able to make accurate predictions for Kondo temperatures and conductance lineshapes. Choosing nitric oxide (NO) as a simple and exemplary spin $1/2$ molecular radical, we present calculations based on a combination of density functional theory and numerical renormalization group (DFT+NRG), predicting a zero bias spectral anomaly with a Kondo temperature of 15 K for NO/Au(111). A scanning tunneling spectroscopy study is subsequently carried out to verify the prediction, and a striking zero bias anomaly is confirmed, still quite visible at liquid nitrogen temperatures. Comparison shows that the experimental Kondo temperature of about 43 K is larger than the theoretical one, whereas the inverted Fano lineshape implies a strong source of interference not included in the model. These discrepancies are not a surprise, providing in fact an instructive measure of the approximations used in the modeling, which supports and qualifies the viability of the density functional theory and numerical renormalization group approach to the prediction of conductance anomalies in larger molecular radicals.

Electron transport through molecules adsorbed on metallic surfaces or suspended between metal leads is the basic ingredient of molecular electronics (1–3). Because the highest occupied and lowest unoccupied molecular orbitals rarely lie close to the Fermi energy, electrons must generally tunnel through the molecule, making the zero bias conductance much smaller than $G_0 = 2e^2/h$, the conductance quantum, whenever gating is not easily achieved, as is the case in mechanical break junctions and scanning tunneling microscopy (STM). This problem does not persist for molecular radicals, where one or more molecular orbitals are singly occupied, generally resulting in a net spin. When brought into contact with a metal, the radical’s spin is Kondo screened (4), leading to a zero bias conductance that may be of order $G_0$, with a Fano-like anomaly below the Kondo temperature $T_K$ (5, 6) and no need for gating. One reason for practical interest in such anomalies is the sensitivity of the conductance to external control parameters such as magnetic fields and mechanical strain (7). Several molecular contacts have been studied (8), involving both adsorbed (9–16) and contact-bridging (7, 17–19) molecules. None so far involved a radical molecule that is both simple and spin $1/2$, and the Kondo anomalies were not predicted from first principles, ahead of experiment. Both the intrinsic complexity of the contact between a large molecular radical and a metal and the unavailability of quantitatively tested ab initio electronic structure-based approaches to Kondo conductance have so far restricted the theoretical work to the role of a posteriori support of STM and break junction zero bias anomaly data. It is therefore important to achieve a first-principles predictive capability of Kondo conductance anomalies across molecular radicals and ascertain its reliability. To that end, we put to work a density functional theory and numerical renormalization group (DFT+NRG) method devised and implemented earlier in our group (20–22) but not yet verified by experiment. Although other strategies with similar goals have also been proposed in refs. 23–26, we can now demonstrate the predictive power as well as the limitations of our procedure in a specific test case where direct comparison with experiment is possible.

Seeking a molecular radical Kondo system of the utmost simplicity and stimulated by the experimentally observed Kondo screening of the $S = 1$ radical $O_2$ (12), we singled out nitric oxide (NO) as the simplest and smallest $S = 1/2$ radical molecule that might display a Kondo conductance anomaly in an adsorbed state. We have therefore applied our theoretical program to STM conductance of the NO radical adsorbed on the Au(111) surface. NO is an interesting test case, in the past only qualitatively considered as a prototype of radical-surface Kondo interactions (27, 28), whereas recently it has been used instead to quench the spin state of larger molecular radicals such as porphyrins (29).

Starting with DFT calculations of an idealized Au(111)/NO/STM tip interaction as shown in Fig. 1, we determined the adsorption geometry and the persistence of a nonzero spin state carried by the $2e^2/|h|$ orbitals of NO. A two-orbital Anderson model describing their hybridization with the gold surface Fermi sea

**Significance**

Molecular electronics, with molecules functioning as the basic building blocks of circuits, is considered by some to be one of the contenders for next-generation electronics. Radical molecules are interesting because a quantum phenomenon, the Kondo effect, involving the radical’s unpaired electron and its spin, has the potential to enhance and control conductance. Examples of molecular Kondo are known experimentally in geometries including mechanical break junctions and scanning tunneling microscopy (STM), but so far it has not been possible to make accurate theoretical predictions. Here we predict the Kondo effect expected for the simplest molecular radical, nitric oxide, on a gold surface. Subsequently we verify that experimentally by STM. Both agreements and discrepancies offer a quantitative lesson of considerable future use.


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Fig. 1. Model STM geometry for NO/Au(111). The scattering region shown contains one NO molecule and 28 Au atoms; it satisfies periodic boundary conditions in the transverse direction and is bounded by two planes in the c direction, where the potential is smoothly matched to the potential of bulk gold. NO is shown in the optimal on-top adsorption geometry, where the molecule is bent by about 60°. Figure produced using VESTA (46).

was constructed and its parameters were adjusted to quantitatively reproduce the DFT results. The NRG solution of the Anderson model (NRG Results) determined which of the two $2\pi^*$ orbitals, namely the one with odd symmetry, is eventually screened at the Kondo fixed point. A spectral function peak and a zero bias conductance anomaly were predicted with a Kondo screened at the Kondo fixed point. A spectral function peak and a zero bias conductance anomaly were predicted with a Kondo screened at the Kondo fixed point. A spectral function peak and a zero bias conductance anomaly were predicted with a Kondo screened at the Kondo fixed point. A spectral function peak and a zero bias conductance anomaly were predicted with a Kondo screened at the Kondo fixed point.

To check these predictions we carried out STM/scanning tunneling spectroscopy (STS) experiments (Experimental STM/STS Results) for NO/Au(111). A clear Kondo anomaly was found with an experimental Kondo temperature of about 15 K [half width at half maximum (HWHM) of 5 meV]. Adopting Wilson’s definition, the Kondo temperature $T_K$ is inferred from $\Delta_{\text{HWHM}} \approx 4.6k_B T_K$ (30), where the HWHM is extracted from the linewidth $\Gamma_k$ obtained from a Frota lineshape fit (31).

To calculate the hybridization of the molecular orbitals with the gold surface, we use the information contained in the calculated phase shifts of gold conduction electrons scattering off the adsorbed molecule (20, 21). The quantum mechanical scattering problem is solved numerically for the geometry in Fig. 1, using pwcond (34) (Materials and Methods), which provides spin-resolved phase shifts for the relevant symmetry channels. Here we focus on two symmetries, namely even ($e$) and odd ($o$) under reflection across the Au$_{\text{top}}$-N-O plane, corresponding to the strongly and weakly hybridized NO $2\pi^*$ orbitals, respectively. Examples of resonances in the phase shifts are shown in Fig. S1.

The next step of our theoretical protocol is to define an Anderson model Hamiltonian including channels of both symmetries,

$$H = e_i n_i + e_o n_o + \sum_{a=e,o} \sum_{\alpha=\text{int}} \left( V_{\alpha a} C_{\alpha a}^\dagger C_{\alpha a} + V_{\alpha o} C_{\alpha o}^\dagger C_{\alpha o} \right) + H_{\text{int}},$$

where the subscript $a=e/o$ stands for the $2\pi^*_a$ state, $V_{\alpha a}$ describes hybridization with gold conduction states, and $H_{\text{int}}$ contains all of the interactions in the $2\pi^*$ manifold. When the molecule is brought down to the surface in an upright configuration at the on-top, fcc, or hexagonal close-packed (hcp) sites, the crystal field lowers the cylindrical symmetry of the isolated molecule to $C_3v$. Further tilting of the molecule at the on-top site breaks $C_3v$ symmetry and lifts the $2\pi^*$ degeneracy. The splitting of the $2\pi^*$ and $2\sigma^*$ levels (Fig. S2) and their unequal hybridization with gold conduction states, at first sight an irrelevant detail, is actually crucial to the Kondo physics, as we discuss below.

The molecular orbitals hybridize with both surface and bulk states. Surface state hybridization affects the electronic structure of adsorption but only weakly. This is borne out in our slab calculations, where the adsorption energy converges already for 5 layers, whereas the energies of the surface states of the top and bottom of the slab—strongly split by their mutual interaction—do not converge until ~23 layers (35). If surface state hybridization had a significant effect on the electronic structure, one
would expect the adsorption energy to converge more slowly than it does. Surface states decay exponentially inside the bulk, and therefore their contribution to the hybridization and phase shifts, and hence to the conductance anomalies, is invisible in our scattering calculations, which involve only bulk scattering channels. We checked that the ab initio estimates of the molecular orbital hybridization linewidths \( 2\Gamma_a = 2\pi \sum_\delta |V_{ka}|^2 \delta(e_k - e_F) \) are well converged with respect to the number of layers of the slab.

The interaction Hamiltonian is now written in terms of the 2\( \pi^* \) states as

\[
H_{\text{int}} = Ue_c n_{\pi^+} n_{\pi^-} + Ue_c n_{\pi^-} n_{\pi^+} + Ue_c n_{\pi^+} n_{\pi^-} + JH_S \sigma_z S_0 \cdot S_0 + W , \tag{2}
\]

where the \( U \) terms are intrachannel and interchannel Hubbard interactions, the \( J_H \) term is their Coulomb ferromagnetic (Hund's rule) exchange interaction, and \( W = W_{\sigma^o c^\dagger_\alpha} c_{\beta} c_{\sigma^o} + W_{\sigma^o c^\dagger_\sigma} c_{\alpha} c_{\sigma^o} \) is a small but nonzero pair hopping term. To fix the model parameters from the first-principles DFT input, we require the scattering phase shifts of the model Hamiltonian at the Hartree–Fock (mean-field) level to reproduce the phase shifts of the ab initio scattering calculation for the full system. The physical picture behind this type of matching is the local moment regime of the Anderson impurity model; because spin-polarized DFT and Hartree–Fock provide comparable mean-field descriptions of the local moment regime, we can reliably infer the model parameters by requiring them to give the same phase shifts. With four total phase shifts from the two channels and two spin polarizations, these conditions determine the four model parameters \( e_c \), \( e_o \), \( U_c \), and \( U_o \). To fix the remaining parameters \( U_{oo}, J_H \), and \( W_o \), we make use of relationships between the interaction parameters that are exact for the isolated molecule (SI Text) and should still apply to the adsorbed molecule owing to its gentle physisorption. The resulting parameters (Table S2) provide all of the ingredients we need for a many body calculation of the spectral function and Kondo conductance anomaly.

**NRG Results**

The two-orbital Anderson model, Eq. 1, is solved by NRG (30, 36, 37); details are given in Materials and Methods. For tilted NO adsorbed at the on-top site, the solution indicates a competition of the ingredients we need for a many body calculation of the spectral function and Kondo conductance anomaly.

**Experimental STM/STS Results**

To verify the theoretical predictions just presented, we carried out STM measurements of NO adsorbed on Au(111). Submonolayer NO was dosed on a reconstructed Au(111) surface at 30 K, and the sample was then cooled to 5 K. STM images acquired with tunneling currents below 10\(^{-11}\) A show that the molecules adsorb preferentially at the fcc elbows of the gold herringbone surface reconstruction as isolated units or small disordered clusters at low coverage—below about 0.05 monolayers—and form large disordered clusters at higher coverage. The images of small clusters in Fig. 3 B and C indicate that the largest proportion of molecules adsorb on top, in agreement with the theoretical prediction. The average nearest-neighbor NO–NO distance in the clusters is about 0.5 nm. After annealing at 70 K, the molecules form ordered islands with a variety of metastable lattices with unit vectors between 0.35 nm and 0.60 nm. The angle between the unit vectors of the molecular lattices and those of the gold surface is between 0° and 30°. The structures either are incommensurate with the substrate or have a large unit cell with several inequivalent molecules, suggesting that the NO–NO interaction prevails over the NO–Au interaction. The NO lattice shown in Fig. 3D is formed by units that have a dumbbell appearance in the filled-state STM images. This shape is consistent with the charge distribution of the 2\( \pi^* \) orbital of the tilted molecule (Fig. 2) and supports the results of the NRG calculations that predict this state is preferentially filled.

STM spectra measured on isolated NO molecules, small disordered clusters, large disordered clusters, and ordered NO lattices all display similar dip-shaped conductance anomalies centered at the Fermi level, as shown in Fig. 3F. For isolated molecules, whose mobility at 5 K was too high to acquire images with enough resolution to detect the predicted on-top adsorption state and tilt angle, the HWHM of the dip is about 12 ± 4 meV at 5 K with an amplitude that is ~25% of the background conductance. For NO clusters and lattices, the dip HWHM is 16 ± 4 meV at 5 K and depends on the position of the molecule. In addition to the zero bias dip, shoulders at ±30 meV are visible in the spectra taken over the isolated molecule but not over clusters (Fig. 3F). We have not been able to determine whether these inelastic features are of...
Fig. 3. STM/STS images and spectra, all obtained with clean Au tips except for B and C. (A) Isolated NO molecules (arrows) and small NO clusters on Au(111) at 5 K. (B and C) Two small NO clusters formed from a few molecules (in the center) and substrate Au atoms (at the edges) imaged with a molecule on the STM tip. The Au lattice is marked by blue dots. Most of the molecules are on top. (Scale bar, 0.5 nm.) (D) Filled-state STM image (V_{bias} = -60 mV) of an ordered single NO layer obtained after annealing at 70 K. The layer is made up of rows of units with a dumbbell shape that is consistent with the shape of the filled 2σσ* orbital. The arrows point to two of these units. (E) NRG spectral functions for the 2πσ orbital of NO at the on-top adsorption site calculated at 5 K with ab initio parameters from Table S2. Inset: spectral function (Left), Fano lineshapes (Upper Right), and interfering tunneling paths t1 and t2 (Lower Right). (F) Tunneling spectra of isolated molecules and small clusters at 5 K and clusters at 40 K and 68 K showing the Kondo dip. The spectra are shifted vertically for clarity. The solid lines are fits with the Frota function (31).

vibrational or electronic origin, but the symmetric displacement of the shoulders with respect to zero bias, as well as their disappearance in clusters, is suggestive of a vibrational origin. By DFT calculations we find vibrational eigenmodes with frequencies of 25 meV and 42 meV in the correct range. Spin transitions and anisotropy are not expected for a spin 1/2. Hypothetically, electronic states might offer an alternative explanation, the lower Hubbard band of the 2σσ* state, visible just below Fermi in the NRG spectra (Fig. 3E), corresponding to the left shoulder, and the empty 2πσ state forming a resonance above Fermi, corresponding to the right shoulder. Altogether, an electronic explanation seems less likely.

No other sharp structures were observed between ~0.8 eV and 0.8 eV from the Fermi level as shown in Fig. S3 and described in SI Text. In particular, the large step at ~0.45 eV corresponding to the bottom of the clean Au(111) surface state band is absent in the spectra measured over molecules, indicating that free surface state electrons are pushed out by the NO molecule, to become detectable again in spectra 1–2 nm away. Although surface states are repelled, nevertheless their tails are expected to extend up to and hybridize with the NO radical.

To further confirm the Kondo nature of the observed zero bias STM anomaly, the temperature dependence of the half width at half maximum of the dip was measured and is shown in Fig. 4. For each temperature, the lineshape was fitted with an asymmetric version (38) of the Frota function (31) with asymmetry parameter φ = π. By 70 K, the HWHM has grown to 40–50 meV and the amplitude has decreased from ~25% to ~10% of the background. Due to the high mobility of the isolate molecules at high temperature and the ensuing difficulty of acquiring spectra for them, all data presented for T > 5 K were taken on NO islands. The effect of the temperature-induced broadening and attenuation of the dip is intrinsic because it is about a factor of 5 larger than the effect of the change of the experimental resolution of STS at high temperature related to the broadening of the Fermi distribution of the tip, corresponding to a HWHM of about 10 meV at 68 K. The large intrinsic broadening rules out inelastic tunneling (vibrational or electronic excitations) as the main origin of the dip. The Kondo temperature ~43 K, extracted from the low-temperature limit of the Frota linewidth parameter ΓK, is about a factor of 3 larger than our unbiased theoretical prediction. This level of discrepancy is not surprising in view of the exponential sensitivity of the Kondo temperature to the impurity parameters and of the self-interaction errors generally affecting the first-principles DFT calculations.

Actually, a theoretical underestimate of the Kondo temperature is not unexpected, because the hybridization with gold surface states, as was mentioned above, is not completely accounted for in our calculations. Despite these deficiencies, the overall, unbiased theoretical results are gratifyingly reproduced, and so is the evolution of the zero bias anomaly with temperature, as shown in Fig. 4. The experimental offset of the center of the dip from the Fermi energy, less than 2 meV, is much less than the width, indicating that the parent level of the Kondo resonance is indeed nondegenerate. That provides an indirect and yet strong confirmation that the NO molecule is tilted, for if the 2πσ levels were degenerate, the Kondo peak would be shifted above the Fermi energy to satisfy the Friedel sum rule (39). The data do not clearly establish whether the symmetry of the Kondo orbital is odd as predicted, and that remains to be verified, e.g., by photoemission spectroscopy.

Finally, the observed Fano conductance lineshape (Fig. 3E, Inset), a q ∼ 0 dip rather than q ∼ ∞ as predicted by the impurity
particularly the need to fully incorporate the metal surface states.

Experimental error bars indicate that direct tunneling into the molecular 2π* states (\(t_1\) in Fig. 3E, Inset) is dominated by another tunneling channel (\(t_2\)). As STS indicates, the NO molecule is fully immersed in the Au(111) surface states, whose wave functions extend far out into the vacuum, reaching out to the STM tip. Because surface states do not represent a bulk screening channel, they are not included in our scattering calculations. Because the surface states are nonetheless involved and provide a free electron reservoir for Kondo screening, their local density of states near the molecule will show a dip at the Fermi energy, complementary to the calculated bare NO spectral function peak. As observed in the Kondo STM conductance anomalies of many other adsorbed magnetic atoms, and as generally discussed by Ujlsaghy et al. (40), \(dI/dV\) spectra are strongly modified, in our case very plausibly dominated, by direct tunneling into nearby metal surface states, specularly reversing the intrinsic Kondo anomaly.

### Conclusions and Outlook

We have described how the Kondo parameters and resulting zero bias STM conductance anomaly of an adsorbed molecular radical can be predicted from first principles, with features that compare reasonably well with those of a subsequent experiment. To do so, we used NO as the simplest spin 1/2 molecular radical capable of forming a Kondo screening cloud when adsorbed on a gold surface. The discrepancies between the calculated Kondo temperature and lineshape, which we did not try to amend in any way, and the measured ones are quite instructive, highlighting in particular the need to fully incorporate the metal surface states in future calculations. The delicate renormalization group flow toward the least hybridized, odd symmetry 2\(\pi^*\) state also appears as an instructive many body effect and remains a prediction to be verified. The magnetic field splitting of the Kondo anomaly, presently academic in view of the large value of \(T_K\), could easily be calculated if need be.

The protocol implemented here for NO/Au(111) in a specific STM geometry is of more general applicability and can be applied to different molecular radicals and different STM and bias junction geometries, where the influence of structural or mechanical deformations could be explored. As an overall result, the DFT+NRG approach demonstrates enough predictive power to be useful in the a priori evaluation of the conductance characteristics of molecular radical nanocavities, thus providing a theoretical asset of considerable technological relevance.

### Materials and Methods

Density functional theory calculations in the generalized gradient approximation of Perdew et al. (41) were performed with Quantum Espresso (42), a plane wave pseudopotential electronic structure package. The NO/Au(111) adsorption geometry was determined using the slab method in a 3 × 3 surface supercell with a vacuum layer of 16 Å. Scattering calculations were carried out with psccsd (34) in a 3 × 3 supercell with a vacuum layer of 8.4 Å, in correspondence with the experimental tip height of ~10 Å. Brillouin zone integrations were performed on a 6 × 6 × 2 k-point mesh with a smearing width of 0.002–0.010 Rydberg. Plane wave cutoffs were 30 Rydberg for the wave function and 360 Rydberg for the charge density. As detailed in SI Text, Hubbard interactions were applied to the states of Au (\(U = 1.5\) eV) and the p states of N and O (\(U = 1.0\) eV).

Numerical renormalization group calculations were carried out with NRG Ljubljana (41), using the z-averaging technique (30), the full density matrix approach (43), and the self-energy trick (44). The logarithmic discretization parameter was chosen to be \(\Lambda = 4\), and a maximum of 2,000 states (not counting multiplications), corresponding to roughly 5,000 total states, were kept at each iteration. Spectral functions were obtained by log-Gaussian broadening (45) and at finite temperature with a kernel that interpolates between a log-Gaussian at high energy and regular Gaussian at low energy (43). The \(dI/dV\) spectra were measured with a clean Au tip by the lock-in technique, applying a 3-mV modulation to the bias voltage and using a maximum current of \(3 \times 10^{-11}\) A to avoid tip-induced modification of the adsorption geometry. NO molecules were easily displaced at higher tunneling currents at 5 K and were mobile at temperatures above 20–30 K. The gold lattice and molecules could be resolved simultaneously only once (Fig. 3B and C), when an unknown molecule adsorbed on the tip. The horizontal stripes in Fig. 3B and C are caused by temporary detachments or shifts of the molecule. The broadening of the tunneling spectra caused by the finite modulation voltage is taken into account in the fit of the measured spectra by calculating the convolution of the Frota function with \(\left(1 - (V/\nu_{FM})^2\right)^{-\frac{1}{2}}\), where \(\nu_{FM}\) is the peak-to-peak value of the modulation voltage and \(V\) is the bias. This function represents the response of the STS spectroscopy with a sinusoidal modulation of the bias and a lock-in amplifier to a delta function-like density of states. The effect of the thermal broadening of the Fermi distribution in the tip at high temperature was taken into account by computing the convolution of the Frota function with the derivative of the Fermi distribution.

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Supporting Information

Requist et al. 10.1073/pnas.1322239111

SI Text

First-Principles Electronic Structure Calculations. Density functional theory calculations of nitric oxide (NO) adsorption were performed using the slab method with three to seven gold layers and a 3 x 3 hexagonal supercell of the unreconstructed Au(111) surface, corresponding to 1/9 monolayer coverage. This cell was large enough to reduce the interaction between periodic images of the NO molecule to a negligible level. Selected calculations were repeated with 2 x 2, 2 x 3 x 3, and 2 x 3 x 2 x 3 cells to verify convergence. The unreconstructed Au(111) surface is expected to be a good approximation to the face-centered cubic (fcc) regions of the well-known 22 x 3 x 3 "herringbone" reconstruction, where the experimental measurements were performed. For calculations of the adsorption energy, the vacuum layer was set to 16.9 Å, whereas for calculations of the scattering phase shifts, it was reduced to 8.4 Å, corresponding to the experimental tip height. The latter value was large enough that the shape of the tip (Fig. 1 of the main text) had a negligible effect on the adsorption geometry and hybridization linewidths. Hence, the scattering calculations were performed without any model for the tip, essentially using the bottom of the slab as a broad distant probe.

The unreconstructed Au(111) surface presents four distinct high-symmetry adsorption sites—fcc, hexagonal close packed (hcp), bridge, and on top. For each site, all of the coordinates of NO and the two highest layers of gold were fully optimized. By subsequently applying constraints to the Au atoms, it was found that only the relaxation of the Au atoms nearest to N had a significant effect on the results, and therefore in the scattering calculations we fixed all Au atoms to their bulk positions, except the one, two, or three Au atoms nearest N in the case of top, bridge, and hollow site adsorption, respectively. At the top site, the Au atoms directly beneath N, which we label Au top, are pulled out of the surface by 0.11 Å, enhancing the interaction between the NO 2π* molecular orbitals and an spd hybrid orbital (mainly d z2) of Au top.

Table S1 summarizes our ab initio results for gas phase NO and NO/Au(111), including the adsorption energy \( E_{ad} \), magnetic moment \( \mu \), NO bond length \( d_{NO} \), AuN bond length \( d_{AuN} \), the stretching frequency \( \nu_{\text{NO}} \), and electric dipole moment calculated with generalized gradient approximation (GGA)+U. The magnetic moment is reported for the entire cell, including the small induced magnetization on gold. The surface-adsorbate electric potential along the z direction at the top site, NO was found to tilt away from the upright configuration, giving a Au top–N–O angle of 122.4°, in agreement with earlier calculations (1). The tilting, which accounts for a large part of the adsorption energy, is crucial for the present study because it alters the Kondo physics by lifting the degeneracy of the 2π* orbitals. The molecule tilts toward one of the six nearest-neighbor surface gold atoms of Au top. For definiteness, we take the molecule to tilt in the positive z direction, so that the tilt plane is the xz plane. The degenerate 2π* orbitals split into two orbitals that we label 2π x and 2π y, according to their symmetry (even or odd) with respect to reflection through the tilt plane. Full geometry optimization shows that the tilt plane undergoes a small azimuthal rotation of 8.6° around the surface normal. The order of magnitude of the calculated adsorption energies agrees with an estimate of 400 meV from temperature-programmed desorption spectroscopy (2) and the results of a comprehensive study (1) of NO adsorption on metal surfaces, although the site dependence differs. We are not aware of any further experimental data for NO/Au (111), but our calculations of the molecule in vacuum (Table S1) are in good agreement with gas phase measurements. The calculated ionization energy of NO, 9.007 eV, is also fairly close to the experimental value 9.27483 ± 0.00005 eV (3). The work function of gold, calculated with a 24-layer slab with 24 Å of vacuum, is 5.19 eV and compares favorably with the experimental value 5.31 eV (3).

In view of the weak adsorption energy, selected calculations were performed with the following four functionals to judge the sensitivity of the results to the choice of exchange-correlation functional: (i) the local (spin) density approximation (LDA) of Perdew and Zunger (5), (ii) the GGA of Perdew et al. (6), (iii) the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional (7), and (iv) a modified version (8) of the Vydrov–Van Voorhis (VV10) functional (9) describing van der Waals interactions. The LDA approximation, known to be overbonding for molecules on surfaces, was found to be inadequate, causing NO to demagnetize. The VV10 functional increased the adsorption energy uniformly for all sites, yielding 540 meV, 380 meV, and 360 meV for the on-top, bridge, and fcc sites, respectively. Hybrid functionals have been found to give good results for the adsorption of small molecules on metal surfaces (10); however, because they open a small gap at the Fermi energy in metals, they are potentially problematic when the molecular levels lie close to the Fermi energy, as they do in our case. Moreover, such a gap would cause artifacts in the calculation of the scattering phase shifts. For these reasons, all of the results reported in the main text were obtained with the GGA and GGA+U.

Hubbard interactions \( U_{NN} = U_{O} = 1 \) eV were applied to the N and O orbitals in the GGA+U scheme to stabilize the magnetic moment. Similar values have been used for CO to correct the adsorption site preference on Pt(111) (11) and Cu(111) and Cu (001) (12). We also used Hubbard interactions to correct the energy of the Au d bands, which in LDA and GGA (13, 14) is too high compared with that in angle-resolved photoemission spectroscopy (15). We found that the value \( U_{Au} = 1.5 \) eV shifts the fully occupied d bands down rigidly by 0.5 eV, bringing them into agreement with experiment and leaving the sp bands virtually unchanged. This value of \( U_{Au} \) was adopted in calculating all quantities in Table S1. The GGA+U scheme has been used in a similar way to correct the d states of Ni in a study of the adsorption of CO and NO/NiO(100) (16, 17).

The projected densities of states for the isolated molecule, the clean surface, and the combined surface–adsorbate system are shown in Fig. S2. The most important observation is that the degeneracy of the 2π x and \( \Gamma_{\pi} \) orbitals is broken by the tilting of the molecule, yet both remain partially occupied. The tilting of the molecule away from the upright configuration increases the hybridization of the 2π x orbital and decreases the hybridization of the 2π y orbital. As reported in Table S2, the hybridization \( \Gamma_{\pi} \) becomes five times as large as \( \Gamma_{\sigma} \) for the optimal tilt angle of nearly 60°.

Despite the substantial tilting of the molecule, there is only a relatively weak symmetry breaking in the 2π* orbital occupations. One might have expected the 2π y orbital to be nearly empty, because its bare energy is pushed up by as much as 0.24 eV due to its antibonding interaction with the spd hybrid orbital of Au top. Instead, it is even more occupied than the 2π x orbital. The 2π x and 2π y molecular orbitals have fractional occupation numbers, \( n_x = 0.65 \) and \( n_y = 0.44 \), adding up to slightly more than 1, consistent with modest charge transfer from the surface to the molecule. The degeneracy of the \( \pi \) orbitals is also lifted by the
tilting, but they split in the opposite direction because they lie below rather than above the $d$ states in energy. The lack of distinct symmetry breaking in the $2\pi_e$ orbital occupations might be a spurious result, possibly caused by self-interaction error, or it might be a genuine consequence of orbital fluctuations. Hubbard interactions in nitrogen and oxygen are unable to induce a stronger symmetry breaking even though they increase the $2\pi_e/2\pi_e^*$ splitting for the spin and orbital symmetry-broken solution in vacuum. It might be possible to achieve orbital symmetry breaking by applying Hubbard-type interactions to molecular orbitals rather than atomic orbitals (cf. ref. 11) or in an approach with inherently less self-interaction error such as reduced density matrix functional theory, but we do not pursue these approaches here.

The Blyholder (18) and Hammer–Morikawa–Norskov (19) models, which describe the adsorption of CO in metals in terms of $\sigma$ donation and $\pi$ back bonding, provide a starting point for understanding the bonding interactions between NO and the gold surface; however, $\sigma$ and $\pi$ are no longer proper symmetries due to the tilting of the molecular axis. Modest back-bonding interactions are visible at the top of the $d$ band (2.5 eV below the Fermi energy) in Fig. S2, coinciding with peaks in the Au$_{top}$ $d_{z^2}$ states. The strong participation of the Au$_{top}$ $d_{z^2}$ states in the $2\pi_e^*$, $5\pi$, $1\sigma_z$, and $4\sigma_m$ molecular orbitals is an important feature of the bonding interaction. There are important differences between the adsorption of NO and that of CO on noble metals, because NO is an open-shell molecule.

**Constructing an Anderson Impurity Model.** An Anderson model representing the hybridization of the $2\pi_e$ molecular orbitals of NO with the Au(111) surface is defined in Eq. 1 of the main text. In specifying the interaction Hamiltonian $H_{int}$, it is convenient to start from the molecule in vacuum. Because the isolated molecule has cylindrical symmetry, the interactions in the $2\pi_e$ sector depend on only two independent parameters and can be expressed as

$$H_{int} = V\frac{N(N-1)}{2} + J_2 S^z L^z,$$  \[S1\]

where $N$ is the total number of electrons, $S$ is the total spin operator, and $L_z$ is the total $z$ component of angular momentum. The two degenerate $2\pi_e$ states, formed from the $p_x$ and $p_y$ orbitals of N and O, can be chosen to be eigenstates of $L_z$; i.e., $|m \pm 1\rangle$. The $|m=0\rangle$ state is not considered because the $p_z$ orbitals, being involved in $\sigma$ bonding, are far lower ($\sim 7.5$ eV) in energy. Because we are considering the symmetry breaking caused by tilting, we express Eq. S1 in terms of the $2\pi_e$ and $2\pi_e^*$ states, which have nodes in the $yz$ and $xz$ planes, respectively. Using the relations $c_{m=1} = (c_x + ic_y)/\sqrt{2}$ and $c_{m=-1} = (c_x - ic_y)/\sqrt{2}$, we find

$$H_{int} = U_{n_\pi} n_{\pi} + U_{\sigma} n_{\pi} n_\sigma + U_{\pi\sigma} n_\pi n_\sigma + J_{1\pi} S_\pi S_\sigma + W + \beta N,$$  \[S2\]

where the $U$ terms are on-site and inter-site Hubbard interactions, the $J_{1\pi}$ term is a Hund interaction ($S_{\pi}$ is the spin operator for the $2\pi_e$ state, not the $\alpha$-component of spin), and $W$ is a double hopping term $W = W_{\pi\pi} n_{\pi}^\dagger c_{\pi} e^\dagger c_{\pi} n_{\pi} + W_{\pi\sigma} n_{\pi}^\dagger c_{\sigma} e^\dagger c_{\sigma} n_{\pi}$. The parameters are uniquely determined by $(V,J)$ according to the formulas $U_{\pi} = U_{\pi} = V + 3J$, $U_{\sigma} = V - J/2$, $J_{1\pi} = 4J$, and $W_{\pi\pi} = 2J$, and $\beta = -J/2$.

When the molecule is brought down to the surface in an upright configuration at the on-top, fcc, or hcp sites, the crystal field lowers the cylindrical symmetry to $C_{3v}$ symmetry. The degeneracy of the $2\pi_e$ states is preserved and Eqs. S1 and S2 remain exact. The tilting of the molecule breaks the symmetry and lifts the $2\pi_e$ degeneracy. The $2\pi_e^*$ orbital evolves into the even $2\pi_e^*$ orbital (Fig. 2 of the main text) that hybridizes strongly with the surface. The $2\pi_e^*$ orbital becomes the odd $2\pi_e^*$ orbital with much weaker hybridization. Eq. S2 remains a valid description of interactions in the $2\pi_e$ sector; however, because the $2\pi_e^*$ and $2\pi_e^*$ orbitals are hybridized with the surface, the interaction parameters will no longer have exactly the same relationship with $(V,J)$ that they have in cylindrical symmetry.

For tilted NO at the on-top site, there were not enough ab initio data to fit all of the parameters in Eq. S2, so we have taken the following strategy. We have fitted the parameters that are most sensitive to the tilting, namely $\epsilon_a$ and $U_{\pi}$, by matching the spin-symmetry broken mean-field $\epsilon_{DFT}$ of the Anderson model to $\epsilon_{DFT}$ inferred from the resonances in the ab initio phase shifts. The hybridization linewidths $2\Gamma_a$ were calculated by fitting the resonances in the scattering phase shifts to the functional form

$$\eta_{DFT}(\epsilon) = \pi \frac{\epsilon}{\epsilon_{DFT}^2} - \frac{\epsilon_{DFT}}{1 + \delta_\epsilon}, \quad [S3]$$

where $\delta_\epsilon$ is a constant shift attributable to potential scattering. An example of the fitting is shown in Fig. S1. The Hund interaction $J_{1\pi}$ was set equal to its value for gas phase NO, and the remaining parameters $U_{\pi}$ and $W_{\pi\pi}$ were assumed to have the same relationship to $V$ and $J$ that they have in cylindrical symmetry (as in gas phase). In this way, all model parameters can be fitted reliably, and we obtain the results in Table S2.

For upright NO at the bridge site, the symmetry is lowered to $C_{\nu}\ldot$. The $2\pi_e^*$ state is defined to be the state that is even/odd with respect to the plane containing NO and the two nearest-neighbor Au atoms. The interaction parameters were approximated the same way as for the on-top site.

Symmetry between the $2\pi_e^*$ states is preserved for upright NO at the fcc site. The interaction parameters were approximated the same way as for the on-top site; however, because the occupied (majority spin) level $\epsilon_{DFT}$ is degenerate and therefore pinned to the Fermi energy, we obtained a more stable fit for $\epsilon_a$ by requiring charge consistency between density functional theory (DFT) and numerical renormalization group (NRG); i.e., $\epsilon_{DFT} = \epsilon_{NRG}$.

**Scanning Tunneling Spectroscopy.** The densities of states measured with a clean Au tip over NO molecules and over the clean Au (111) surface several nanometers away from the molecules are shown in Fig. S3 for an extended energy range around the Fermi energy. The step at about $-0.45$ eV on the gold surface marks the bottom of the surface state band (20). The surface states cannot be detected on top of the NO molecules and gradually vanish when the tip approaches the molecules. The only sharp feature in the NO spectrum above the noise level is the zero-bias dip. The broad and weak bumps at about $-0.15$ eV and $0.3$ eV approximately coincide with the shoulders of the spectral functions of Fig. 3F of the main text.

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Fig. 51. Examples of resonances in the scattering phase shifts with fits to Eq. S3 (Lower) and corresponding peaks in the density of states (DOS) (Upper).
Fig. S2. (A–C) Projected density of states of (A) gas phase NO, (B) three-layer Au(111) slab, and (C) NO/Au(111) slab system. Energies have been shifted to align the vacuum levels of all systems; vertical red lines indicate the respective Fermi energies. Artificial Gaussian broadening of 0.10 eV is used. NO 2p_x and 2p_y orbitals are degenerate in gas phase. The densities of states of the 2π* orbitals are calculated from weighted sums of N and O p_x and p_y orbitals, corresponding to the tilting.

Fig. S3. STS spectra taken over NO molecules at 70 K (thick lines) and over the clean Au(111) surface a few nanometers away at 5 K (thin line).
### Table S1. Ab initio properties of gas phase NO and NO/Au(111)

<table>
<thead>
<tr>
<th>Site</th>
<th>Configuration</th>
<th>$E_{ads}$ (eV)</th>
<th>$\mu_B$, Å</th>
<th>$d_{NO}$, Å</th>
<th>$d_{AuN}$, Å</th>
<th>$\nu_{NO}$, cm$^{-1}$</th>
<th>Electric dipole, $D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase</td>
<td>—</td>
<td>—</td>
<td>1.00</td>
<td>1.1662</td>
<td>—</td>
<td>1,885</td>
<td>0.109</td>
</tr>
<tr>
<td>On top</td>
<td>Tilted</td>
<td>0.320</td>
<td>0.89</td>
<td>1.1704</td>
<td>2.3309</td>
<td>—</td>
<td>(1.148)*</td>
</tr>
<tr>
<td>Bridge†</td>
<td>Vertical</td>
<td>0.148</td>
<td>0.94</td>
<td>1.1653</td>
<td>2.8206</td>
<td>—</td>
<td>0.313</td>
</tr>
<tr>
<td>fcc‡</td>
<td>Vertical</td>
<td>0.122</td>
<td>1.14</td>
<td>1.1688</td>
<td>2.8576</td>
<td>—</td>
<td>0.172</td>
</tr>
</tbody>
</table>

*Experiment, ref. 1. †Experiment, ref. 2. ‡Metastable configuration.


### Table S2. Anderson model parameters for NO/Au(111)

<table>
<thead>
<tr>
<th>Site</th>
<th>$\epsilon_0$</th>
<th>$\Gamma_0$</th>
<th>$\Gamma_0^e$</th>
<th>$U_e$</th>
<th>$U_o$</th>
<th>$U_{eo}$</th>
<th>$J_H$</th>
<th>$W_{eo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>On top</td>
<td>−0.92</td>
<td>−1.02</td>
<td>0.33</td>
<td>0.068</td>
<td>2.24</td>
<td>2.04</td>
<td>1.67</td>
<td>$-0.807$</td>
</tr>
<tr>
<td>Bridge</td>
<td>−1.22</td>
<td>−1.83</td>
<td>0.12</td>
<td>0.13</td>
<td>2.01</td>
<td>3.18</td>
<td>2.13</td>
<td>$-0.807$</td>
</tr>
<tr>
<td>fcc</td>
<td>−1.00</td>
<td>−1.00</td>
<td>0.22</td>
<td>0.22</td>
<td>2.45</td>
<td>2.45</td>
<td>1.83</td>
<td>$-1.06$</td>
</tr>
</tbody>
</table>

All quantities are in electronvolts; SDs of $\epsilon_0$, $\Gamma_0$, $\Gamma_0^e$, and $U_o$ for the on-top site are 0.04, 0.01, 0.036, and 0.015, respectively.