Localized Molecular Constraint on Electron Delocalization in a Metallic Chain

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An artificial quantum structure consisting of a single CO molecule adsorbed on a Au chain was assembled by manipulating single Au atoms on NiAl(110) at 12 K with a scanning tunneling microscope (STM). The CO disrupts the delocalization of electron density waves in the chain, as it suppresses the coupling between neighboring chain atoms. The possibility to specify the CO position on the chain allows controlled modification of the electronic properties in a quantum system. Inelastic electron tunneling spectroscopy with the STM provides vibrational characterization of the adsorbed CO.

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Molecular adsorption on confined metallic systems is one of the key processes in heterogeneous catalysis. The specific adsorption behavior of small metal particles has been attributed to distinct properties of the bare particles, such as electron quantization effects and different binding sites on their irregular surfaces [1]. The intrinsic cluster properties are, however, strongly affected by molecular adsorption [2,3]. Adsorbate-induced modifications of an electronic system are also the crucial requirement for chemical sensing, which relies on changes in conductance induced by interaction with selected gases [4–6]. Both applications demand a profound characterization of the electronic structure of a nanoscale system affected by molecular adsorption.

The use of nonlocal surface science techniques on single crystals and cluster ensembles revealed the damping of surface states and the emergence of additional adsorbate-induced features [7,8]. However, statistical disorder and size effects in cluster ensembles often prevent a determination of adsorbate influences on individual metal aggregates. In experiments with size-selected clusters, dramatic changes in the cluster electronic properties were observed during adsorption of molecular gases [9,10].

Ensemble effects can be circumvented by local experimental techniques, which are sensitive to the atomic structure of an adsorption system [11]. Scanning tunneling spectroscopy (STS) has been employed to measure electronic properties of bare metal clusters, but could not determine the effect of gas adsorption on their electronic system [12,13]. These experiments are especially complicated, as the precise cluster geometry, the number of adsorbed molecules, and their adsorption sites are usually unknown. To reduce the complexity of a metal-adsorbate system, artificial nanostructures were used in the present experiments to investigate adsorbate-induced modifications in a confined electronic system. The study benefits from the well-defined electronic structure of Au chains, assembled on a NiAl(110) surface by atom manipulation techniques [14]. The adsorption of a single CO molecule strongly alters the delocalization of electronic states in Au chains, thus demonstrating the significant electronic effects of molecular adsorption on a quantum system. The choice of the Au/CO system was additionally motivated by the unexpected catalytic activity of Au nanostructures in the low-temperature combustion of CO, attributed to the presence of discrete electronic levels in the Au aggregates [15,16].

The experiments were performed in an ultrahigh vacuum scanning tunneling microscope (STM) operated at 12 K [17]. NiAl(110) was prepared by cycles of Ne^+ sputtering and annealing to 1300 K. STM topographic images reproducibly showed the alternation of Ni and Al rows of the alloy surface. Isolated Au atoms were deposited at 12 K by gold evaporation from an alumina crucible. The preferential Au adsorption site was determined as the bridge position on Ni rows. Single Au atoms could be moved across the surface at small gap resistance ($V_{\mathrm{sample}}/I < 150$ kΩ). Increasing the resistance above 1 GΩ provided stable conditions for imaging and analysis of Au aggregates. The surface was exposed *in situ* to small dosages of CO. The higher CO sticking probability to single Au atoms led to the formation of Au monocarbonyls (AuCO), leaving the NiAl surface nearly free of adsorbates. The Au-CO bond formation drastically decreases the apparent height of Au atoms from 2.5 to 1.2 Å in STM images taken at 2.0 V sample bias [18]. The height contrast was used to estimate the Au/AuCO ratio on the surface.

Two methods were adopted to prepare larger Au/CO adsorption systems on NiAl(110). Au chains in the [001] direction could be assembled from single atoms first, followed by exposing the surface to CO. As Au aggregates proved to be more inert than isolated atoms, a relatively high CO dosage was required to adsorb a single molecule on a chain. In an alternative approach, AuCO species were formed by CO exposure on isolated atoms, followed by the construction of Au chains around a AuCO. Both techniques gave the same results; however, the latter approach enabled control of the CO position on the Au chain and was therefore preferentially used in the experiments. The presence of a CO molecule led to

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distinct changes in the appearance of the Au chain in topographic STM images (Fig. 1). Below 0.5 V sample bias, the molecule is identified as a small protrusion on the chain. Above 1.0 V, the CO causes a distinct dip in the uniform chain height. Estimating the position of the CO-induced feature with respect to the chain atoms indicates the on-top position as the preferential adsorption site. Tunneling at high bias and current conditions ($V_{\text{sample}} > 2.0$ V, $I > 1.0$ nA) triggered a movement of the CO molecule along the chain. The displacement always occurred from the chain interior to the ends, suggesting a higher binding energy at the outermost atoms.

The electronic effects of CO adsorption on Au chains were characterized by STS. The dI/dV signal provides a measure of the density of states of the sample surface. Bare Au atoms on NiAl(110) exhibit a dI/dV resonance at 2.0 V [14]. The unoccupied state was identified by density functional theory calculations as the hybridization between Au $6sp$ and NiAl electronic states, localized in a pseudogap of the NiAl bulk bands [19]. The monomer resonance splits into two and three states in Au dimers and trimers. The construction of Au chains along a Ni trough induces the formation of a 1D quantum well with several quantum well states (QWS) E_n aligned on a free-electron-like band. The band is characterized by an onset at 0.68 V and an effective mass of 50% of the free-electron mass [14]. Wave functions in the well are approximately sinusoids with $n - 1$ nodal planes for the nth QWS.

CO adsorption on Au monomers removes the characteristic dI/dV peak at 2.0 V, accounting for the observed height difference with respect to bare Au atoms in STM topographies [18]. The effect of CO bonding on longer chains is demonstrated by dI/dV spectra of bare and CO-covered Au_7 chains (Fig. 2). The electronic properties of bare Au_7 are characterized by a series of QWS localized at $E_1 = 0.75$ eV, $E_2 = 1.1$ eV, $E_3 = 1.6$ eV, and $E_4 = 2.4$ eV [20]. The adsorption of a single CO at the 5th chain atom removes the electronic resonances and leaves a nearly flat dI/dV spectrum at the position of the molecule [Fig. 2(b), No. 5]. Three QWS dominate the conductance of the four-atom segment on one side of the CO, with energies of $E_1 = 1.0$ eV, $E_2 = 1.7$ eV, and $E_3 = 2.5$ eV. In the two-atom unit on the opposite side, a dI/dV doublet is identified with peaks at 1.5 and 2.3 V. A comparison with the dI/dV signatures of bare Au_2 and Au_4 suggests an electronic division of the Au_7 chain into these two segments due to CO adsorption on the 5th chain atom. A similar behavior was found for different CO positions and chain lengths. For example, binding of a CO molecule to the center atom of Au_{11} splits its electronic structure into two Au_5 chains separated by AuCO.

The spatial distribution of QWS in Au chains and the symmetry of the underlying wave function can be visualized in dI/dV microscopy images, mapping the dI/dV signal at constant bias across the chain. Figure 3(a) shows dI/dV images for a bare Au_{11} chain, taken at the positions of the lowest five QWS [21]. Because of the small energy separation of E_1 and E_2, two wave functions contribute to the dI/dV image at 0.9 V, obscuring the symmetry of the pure states. The 3rd QWS dominates the conductance at 1.3 V; the associated wave function is clearly identified by its two nodal planes. Images at 1.7 V and 2.1 V show three and four dI/dV minima along

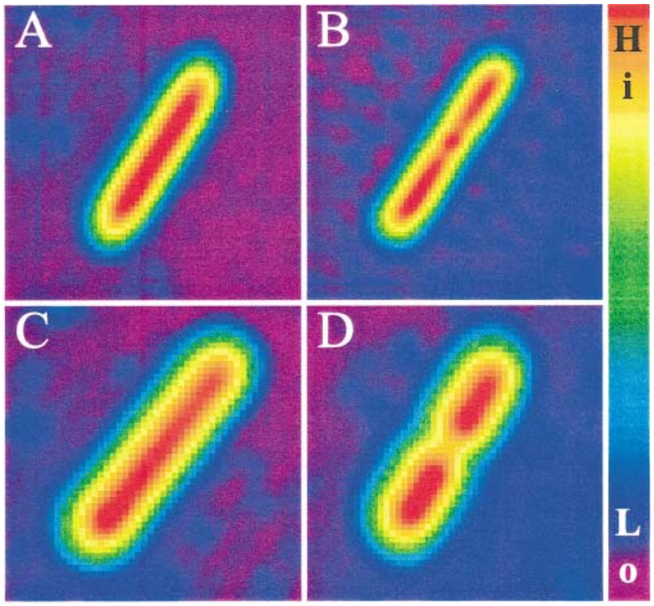

FIG. 1 (color). STM topographic images of (a),(c) a bare Au_{11} chain on NiAl(110) and (b),(d) a Au_{11} chain with a single CO molecule adsorbed at the 6th atom (image sizes 50 Å × 50 Å). Images were taken at 0.1 nA and 0.1 V (a),(b) and 2.0 V (c),(d).

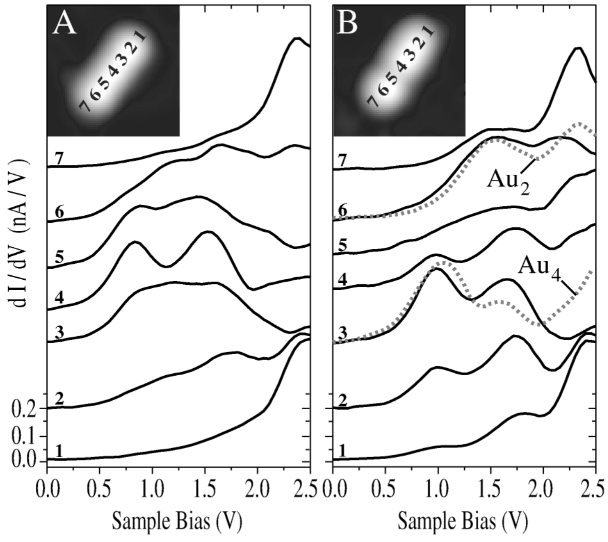

FIG. 2. dI/dV spectra of (a) a bare Au_7 chain and (b) a Au_7 chain with a single CO molecule adsorbed on the 5th atom, taken at positions indicated in the insets. The broken lines in (b) show spectra of bare Au_2 and Au_4 chains for comparison. The tunneling gap was set at $V_{\text{sample}} = 2.5$ V, $I = 0.1$ nA.

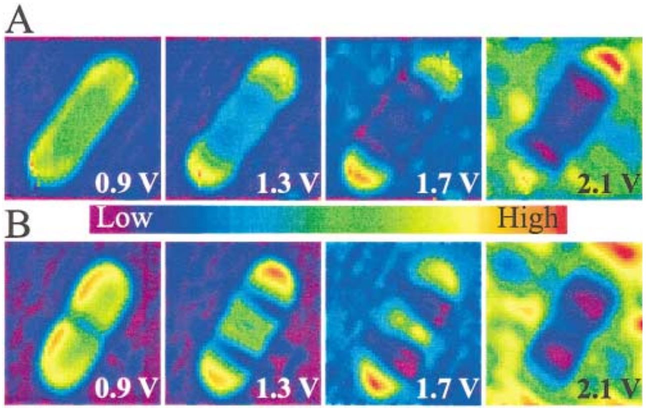

FIG. 3 (color). dI/dV microscopy images of (a) a bare Au_{11} chain and (b) a Au_{11} chain with a CO molecule adsorbed on the 6th atom, taken at indicated sample bias (image sizes 50 Å × 50 Å, $I = 0.1$ nA).

the chain axis, in agreement with the number of nodal planes in the wave functions of E_4 and E_5 [22].

Adsorption of a single CO at the chain center disturbs the characteristic wave patterns of Au_{11} [Fig. 3(b)]. At low sample bias, the chain disintegrates into two parts, replacing the delocalized ground state by states confined in both halves of the chain. No pure energy levels of $Au_{11}CO$ are imaged at 1.3 and 1.7 V. The dI/dV images are dominated by the 2nd QWS in the Au_5 segments at 1.45 V, and reveal the single nodal plane of the corresponding wave function. As one boundary of each Au_5 unit is formed by AuCO, the wave function is slightly asymmetric with the nodal plane shifted toward the chain center. The dI/dV image at 2.1 V represents a mixture of the 2nd and 3rd QWS in the Au_5 segments and shows no well-defined symmetry.

The observed behavior can be rationalized by the Blyholder model, which describes CO bonding to a single transition metal atom [23]. In the most general case, the bond formation results from a charge donation from the CO-5σ orbital into empty sp-like states of the metal and backdonation from d-like metal states to the antibonding CO $2\pi^*$ orbital. The large energy separation of Au d states from the Fermi level disfavors the backdonation in AuCO and leaves the Au $6s$–CO 5σ interaction as the decisive binding mechanism [24,25]. In the presence of the NiAl substrate, the CO adsorption involves the 2.0 V sp-like resonance in the Au adatom and changes its energy position and symmetry. Because of the Pauli repulsion induced by CO orbitals, the new hybrid state is spatially more confined and becomes undetectable in STS [26]. The different energies and symmetries of the unperturbed and the CO-affected Au state prevent the coupling between bare and CO-covered Au atoms. Consequently, the chain breaks into two independent electronic systems. The CO interacts predominantly with a single atom and not with the electronic entity of the chain. However, CO adsorption modifies the band structure of Au chains, as it confines electronic states into the two segments separated by the AuCO. The resulting increase in total energy of the Au/CO system is reflected in the reduced CO sticking probability on Au chains compared to single atoms. The energy cost of breaking the electronic integrity of the chain is reduced when CO adsorbs at the outermost atoms, leaving a large section of the chain unaffected. The CO adsorption on end atoms is therefore stronger than in the chain center, which is consistent with the experimental observation that CO can be induced by tunneling electrons to diffuse to the end of the chain where it is stabilized against diffusion toward the center.

Vibrational properties of the Au/CO chains were investigated by inelastic electron tunneling (IET) spectroscopy with the STM [27]. A series of IET spectra for a Au_7 chain with CO adsorbed on the 5th atom is shown in Fig. 4(a). Whereas spectra taken over bare chain atoms are relatively flat except around the zero bias [28], pronounced features at ±37 mV emerge at the CO position. The signal is attributed to the CO hindered rotation, as this vibrational mode exhibits the largest cross section for adsorbed CO in STM-IETS [29]. The position of the AuCO hindered rotation fits well between literature values for the hindered translation (22 mV) and the external

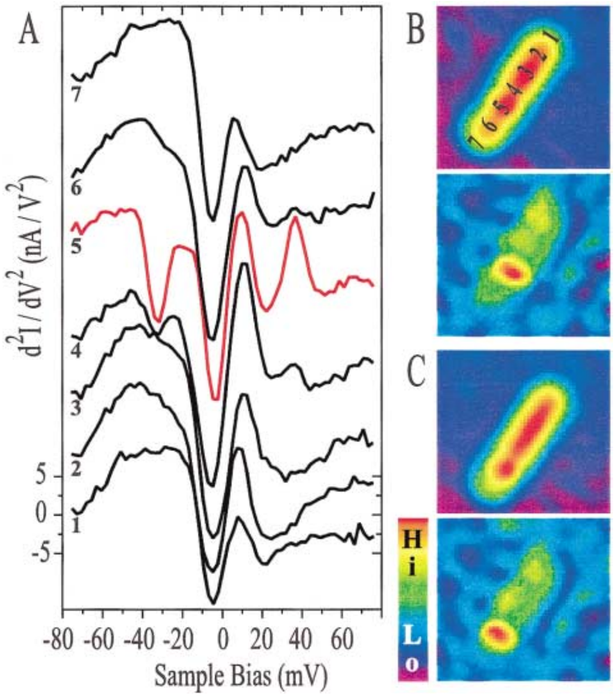

FIG. 4 (color). (a) Vibrational spectra of a Au_7 chain with a CO molecule adsorbed at the 5th atom, taken at the positions indicated in (b). The tunneling gap was set at $V_{\text{sample}} = 0, 1$ V, $I = 0.1$ nA. Topographic and vibrational images of a Au_7 chain with a CO molecule adsorbed on (b) the 5th atom and (c) the 7th atom (image sizes 45 Å × 45 Å, $V_{\text{sample}} = 37$ mV, $I = 1.0$ nA).

CO stretch mode (43 mV) [25]. A slightly lower energy of 34 mV was measured for the hindered rotational mode in isolated AuCO on NiAl(110) [18]. No change in vibrational energy was resolved for CO adsorbed in the interior and at the ends of Au chains. Vibrational microscopy, mapping the IET signal at the vibrational energy, unambiguously reveals the position of the CO molecule on the Au chains. Figures 4(b) and 4(c) show topographic and vibrational images of Au_7 chains on NiAl(110) with a CO molecule adsorbed on the 5th and 7th atom, respectively. At +37 mV, the molecules appear only as faint protrusions in the topography, but clearly dominate the IET image of the Au chains.

The binding of a single CO molecule inhibits the development of delocalized electronic states in artificial Au chains on NiAl(110), as it removes the Au resonance mediating the coupling between chain atoms. The adsorption of a single CO molecule in the chain breaks it into two independent electronic systems. The position of the CO along the chain is precisely controlled. These results emphasize the influence of an adsorbate on the electronic properties of a confined quantum system and provide new insights into the elementary processes associated with chemical sensing and heterogeneous catalysis.

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