Adsorbate-Substrate Vibrational Modes of Benzene on Ag(110) Resolved with Scanning Tunneling Spectroscopy

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Using a low temperature scanning tunneling microscope, we have detected low energy adsorbate-substrate (external or frustrated) vibrational modes of benzene molecules adsorbed on a Ag(110) surface. We demonstrate that such vibrations represent a fingerprint of the molecules' chemical state and environment; two different vibrational spectra are measured on molecules populating two different adsorption states. We also find that the distortion of the adsorption geometry of the molecules may give rise to the excitation of additional (initially hidden) modes. Important differences in the spatial distribution of the inelastic signal are also observed for these external modes.

Vibrational spectroscopies, like infrared absorption spectroscopy (IRAS), helium atom scattering, Raman spectroscopy, or electron energy loss spectroscopy, identify adsorbed species and characterize their chemical environment. Recently, Stipe and co-workers demonstrated that scanning tunneling spectroscopy can also resolve adsorbate vibrations in single molecules [1] by the detection of inelastic scattering processes of the tunneling electrons. This represented a major achievement, since the vibrational fingerprint of an adsorbate allows the chemical characterization of single adsorbates with a scanning tunneling microscope.

Previous inelastic scanning tunneling spectroscopy (ISTS) studies have demonstrated the ability to resolve both internal vibrations [like the ν(CH) mode of C_2H_2 on Cu(100) [1]], and external or frustrated vibrational modes of an adsorbed molecule [like the T and R modes of CO on Cu(100) [2,3]]. The internal modes are typically used in surface chemical analysis for the identification of adsorbed species. On the other hand, the external vibrations are more sensitive to the interaction of the adsorbed molecule with the substrate, since they are directly related to the potential energy surface [4]. Therefore, the resolution of these modes with ISTS gives access to local (site-dependent) information of their adsorption processes as well as provides a valuable tool for the analysis of adsorbate-adsorbate interactions. These external modes generally have lower energy than the internal ones, and are not easily accessed by some of the vibrational spectroscopies mentioned above.

We have resolved adsorbate-substrate vibrations of single benzene molecules adsorbed on a Ag(110) surface with ISTS. We succeeded in measuring significant differences in the vibrational spectra for molecules populating different adsorption states, which probes the strong dependence of these vibrational modes on the chemical environment of the adsorbate. We also report for the first time a site-dependent analysis of the ISTS spectra from which we deduce that the symmetry of the adsorbed

molecule may be essential to understand the origin of missing modes in the spectrum. Accordingly, for each vibration we observe a different spatial distribution of the vibrational signal along a molecule, which points toward different excitation mechanisms.

The experiments were done with a low temperature scanning tunneling microscope (STM) operating in ultra-high vacuum [5]. All spectroscopic data presented were acquired at 4 K, the temperature at which our instrument reaches its maximal stability. However, benzene dosing and initial STM imaging were done with the sample at higher temperatures, to be able to analyze the relative populations of the different adsorbed states. The Ag(110) single crystal was cleaned by repetitive cycles of Ar^+ sputtering and annealing to 800 K. Benzene dosing was done by backfilling the main room-temperature chamber and letting the gas flow to the STM chamber, inserted in a liquid He cryostat.

At a sample temperature of about 30 K benzene on Ag(110) populates a chemisorption state, and is imaged as a circular depression by the STM (Fig. 1a). By injecting electrons with sufficient energy [6] we can pick up a benzene molecule, which placed at the tip apex may produce a substantial enhancement of the atomic corrugation in the STM image [7]. Under these conditions, we determine that the benzene molecule binds on top of a silver atom (see inset of Fig. 1a). As for many other metal systems [8,9], we expect the benzene molecules to lie flat when adsorbed on a terrace.

For the acquisition of a vibrational spectrum, we place the STM tip over the center of a particular benzene molecule and proceed as in the "parent" technique IETS (inelastic electron tunneling spectroscopy [10]). Ramping the sample bias V_s in open feedback loop conditions, we measure the second harmonic of the tunneling current when a small modulation (typically 4 mV rms) is added to the dc sample bias (V_s). This quantity, essentially proportional to d^2I/dV^2, shows a sudden peak-shaped increase whenever the energy of the tunneling electrons reaches
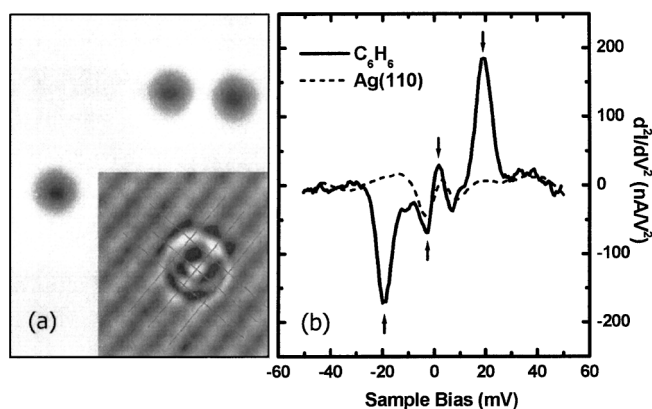
FIG. 1. (a) STM image of chemisorbed benzene molecules deposited on Ag(110) at 30 K (3.9×5.2 nm^2, $I = 1.6$ nA, $V_s = 0.1$ V). The scaled inset is included to indicate the adsorption site ($I = 2.5$ nA, $V_s = 0.15$ V). (b) d^2I/dV^2 spectra acquired on top of a single benzene molecule (continuous line) and on the bare silver surface (dashed line). Both are the average of six scans [$I = 1.6$ nA, $V_s = 0.1$ V, bias modulation (V_{ac}) = 3 mV rms at frequency (f_{ac}) = 341 Hz]. The peaks at ± 4 mV and ± 19 mV represent a change of the junction conductance of about 1% and 8%, respectively.

the onset energy of a vibrational excitation of the adsorbate. Figure 1b shows the characteristic vibrational spectrum measured for a chemisorbed benzene molecule on Ag(110). Two peaks at 4 and 19 mV are observed at both positive and negative bias. The energies of these excited modes are well below the expected values for internal vibrations of benzene adsorbed on a sp-metal surface [on Al(111) the lowest energy of an internal mode is 50 meV, corresponding to a ring deformation mode [9]]. Therefore, we attribute the peaks in Fig. 1b to the excitation of vibrations of the benzene molecule with respect to the silver surface.

The external vibrations in Fig. 1 are characteristic of this state of benzene on Ag(110). To demonstrate the significance of this association we have compared these spectra with those of benzene in a very different adsorption state. Reduction of the sample temperature below 20 K during the benzene exposure promotes the population of an adsorbed state in which the molecules interact weakly with the substrate. These benzene molecules appear in the STM images as protruding features and are easily movable even at 4 K. The vibrational spectra of these weakly adsorbed species (Fig. 2) could be acquired after growing them in a dense hexagonally ordered monolayer thus blocking their movement (see inset of Fig. 2 [11]). Two low energy inelastic peaks are also observed but now at the clearly different values of 7 and 44 mV. These peaks are also due to the excitation of adsorbate-substrate vibrations since they also were observed for single molecules in the same adsorption state that are pinned at positions near steps [12]. Such different values do not necessarily correspond to the same eigenmodes as those observed on chemisorbed benzene. These differences in the spectra of both adsorption states verify the sensitivity ISTS to the chemical environ-
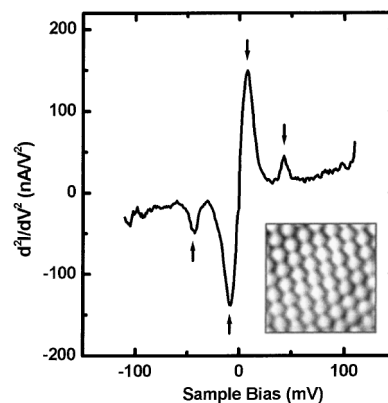

FIG. 2. d^2I/dV^2 spectra acquired on a benzene monolayer grown at 4 K (STM image shown in the inset; 2.5×2.5 nm^2, $I = 0.1$ nA, $V_s = 100$ mV). These species are in a very weak adsorbed state. The spectra is the average of 100 scans ($I = 1$ nA, $V_s = 0.05$ V, $V_{ac} = 5$ mV rms at $f_{ac} = 341$ Hz). The peaks at ± 7 mV and ± 44 mV represent a change of the junction conductance of about 6% and 1%, respectively.

ments of an adsorbate by means of the resolution of its external vibrations.

As mentioned in the introduction, the interest in external vibrations of adsorbates arises from their sensitivity to changes of the adsorbates' local bonding configurations and environments. We have followed the behavior of the chemisorbed benzene molecules as they interact with surface defects by measuring the vibrational spectra on molecules close to step edges. We observed an unexpected feature when the molecules are stabilized [13] at (or close to) substrate atoms forming the corner part of kink sites (K site in Fig. 3a). In Fig. 3b we present the typical spectrum of one such molecule together with that of a nearby molecule on the terrace. Benzene molecules adsorbed at this K site exhibit an additional peak at 39 mV, associated with an external vibration which is not visible in the spectra of molecules at other sites. This additional peak is followed by a negative part, thus closely resembling a Fano line shape [14]. The shape and position of the peaks at 4 and 19 mV remain the same as in the spectrum on molecules at the terrace sites.

The molecules adsorbed at these K sites are imaged by the STM with a characteristic asymmetric shape (Fig. 3a). Therefore, we can correlate the observation of an additional peak in their vibrational spectra with a slight distortion of their adsorption geometry due to their interaction with a nearby kink site. In particular, we hypothesize that the molecules tilt slightly out of their planar geometry, as has been previously suggested from near-edge x-ray–absorption fine structure studies of this system [15]. The symmetry reduction of the adsorption geometry might enable additional inelastic processes to become visible in ISTS. In a similar manner, Lauhon and Ho [16] observed the appearance of an internal vibration of C_6H_6 upon dissociation into C_6H_4, which was also associated with a change in the adsorption geometry of the fragmented benzene molecule.
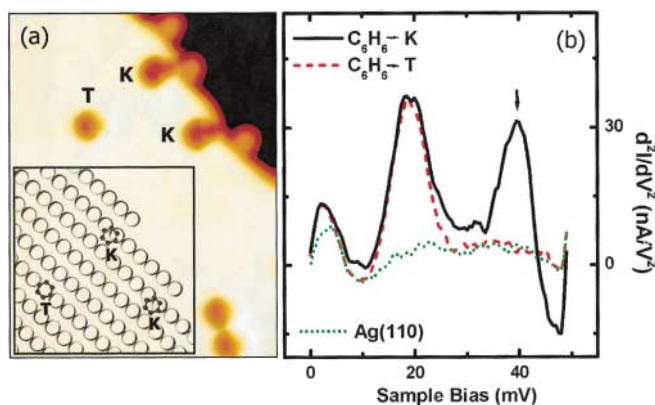
FIG. 3 (color). (a) STM image of benzene molecules deposited on Ag(110) at 20 K (7×5.4 nm^2, $I = 1.6$ nA, $V_s = 0.1$ V). Scaled as the image, a model with the proposed location of the labeled molecules is superimposed. (b) Comparison of d^2I/dV^2 spectra acquired on a benzene molecule at the site labeled K in (a) with the one on the neighbor molecule (T). Background spectra on the bare surface is added with a dotted line. (Each spectrum is the average of six scans, $I = 2$ nA, $V_s = 0.1$ V, $V_{ac} = 4$ mV rms at $f_{ac} = 641$ Hz). The protrusions at the bottom part of the step correspond to benzene molecules which are starting to populate the low temperature adsorption state [12].

To understand, however, the negative values of the inelastic signal [17] appearing for this vibration we have to refer to theoretical descriptions of ISTS. Two theoretical studies predict potential negative contributions to the conductance at the threshold energy of an inelastic process [18,19], namely the excitation of a vibrational mode. Using different approximations, both theories find that the inelastic contribution to the conductance always gives rise to a positive peak in the second derivative of the current vs bias voltage, whereas structures with negative contributions occur at the same energy in the elastic channel. The latter are caused by the interference of electron states, which correspond to direct tunneling on the one hand and the excitation and reabsorption of virtual molecular vibrations on the other. Depending on which of the contributions prevails, a variety of line shapes can appear in the spectra whereby the interference effect gives rise to a Fano-like profile. Following the recent work of Lorente and Persson [19], the relative amount of both contributions depends (quadratically) on the coupling between electronic states and vibrations. This is consistent with our observations of negative values of d^2I/dV^2 for the molecules at the K sites. There the distortion of the adsorption geometry of the molecule may modify the electron-vibration interactions for the additional mode and thus enhance the elastic channel contributions.

Another possible mechanism giving rise to a Fano line shape in vibrational spectroscopies is connected with the energy relaxation due to excitation of electron-hole pairs. This effect has been observed for external vibrations of some adsorption systems with IRAS [20]. The strength of the effect has been shown to depend on both the energy po-

sition of the discrete vibrational excitation relative to the continuum of the substrate excitations and their coupling strength. The adsorption of a molecule close to the kink site may specially enhance the latter, opening a new channel for the energy relaxation. Because of the generality of this kind of process it cannot be ruled out as the origin of the observed feature.

Both findings, the observation of additional vibrational modes and the negative values of d^2I/dV^2, represent characteristics by which the vibrational spectrum of an adsorbate can reflect changes in the adsorption site and geometry. Our data suggest the importance of symmetry in selection rules for ISTS. Determining these selection rules will require further experimental and theoretical investigations.

Finally we are concerned with the spatial distribution of the inelastic tunneling signal associated with external vibrations. For intramolecular modes, the signal is very localized at the position of the particular bond excited [16,19,21]. In our investigation, we have found that the inelastic features of the external modes show characteristic distributions over the whole area of the molecule. Importantly, we have observed striking differences in the spatial "shape" of the three external modes detected on a chemisorbed molecule. This is illustrated in Fig. 4, where the value of d^2I/dV^2 is represented in a color scale as a function of bias energy (vertical axis) and the position
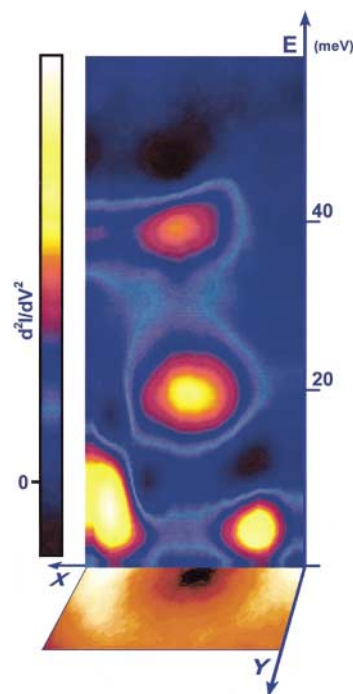

FIG. 4 (color). Two dimensional color scale representation of the d^2I/dV^2 signal as a function of the energy and the distance along one line crossing a benzene molecule at a K site. The line is perpendicular to a [100]-oriented step edge, which is located at the left side. For clarity, in the bottom image we represent the scaled topography of the measured molecule ($I = 2$ nA, $V_s = 0.1$ V, $V_{ac} = 4$ mV rms at $f_{ac} = 641$ Hz).

along a line crossing the molecule at a K site. We observe that the peak at 19 mV has its maximal intensity on the center of the molecule and its spatial width at half maximum is 4.2 Å. This is larger than the molecular dimensions, but still smaller than the characteristic width of the apparent depression in the STM images (typically 6.4 Å width at half minimum). Also the peak at 39 mV is centered above the adsorbate with a slightly narrower spatial width: 3.4 Å. Above this peak, the negative signal appears with a similar shape.

These bell-shaped distributions contrast with the shape of the mode with the lowest energy. In this case, the vibrational signal is very weak at the center of the topographic feature, representing a value of $\delta G/G$ smaller than 1%, but has stronger intensity at both sides of the molecule up to about $\delta G/G \sim 10\%$. The distance between both maxima is 6.4 Å, and thus the maximal intensity is obtained with the tip outside the molecular ring. The different shape of the spatial distribution of these modes, which are only 15 meV apart, induce us to propose that the excitation mechanism of each vibration may not be exactly the same. Additionally, from this particular distribution we can also identify the 4 meV peak with the frustrated translational $[T(C_6H_6\text{-Ag})]$ mode, since we expect that this is the external vibration that preferably affects the tunnel conductance when the tip is displaced from the center of the molecule [19]. Moreover, we find that the energy of this vibrational mode is almost coincident with the energy of the shear-horizontal phonon of the Ag(110) surface (~ 3.5 meV at the boundary of the Brillouin zone) which is essentially confined to the topmost atomic layer [22]. Coupling of these two vibrations, the local molecular and the phonon mode, is very likely.

At this stage the assignment of the other two features cannot be accomplished from our experimental results. Tentatively, we would assign the peak at 19 mV as one of the frustrated rotational modes $R(C_6H_6\text{-Ag})$, and the third spectral feature, at 39 mV, as the perpendicular stretch mode $Z(C_6H_6\text{-Ag})$.

In conclusion, we have observed the vibrations associated with the interaction of a benzene molecule with a Ag(110) surface using a low temperature STM. These vibrations are found to be strongly sensitive to the adsorption properties. On the one hand, we have observed substantially different vibrational patterns for species depending upon the nature of the molecule-substrate bond. On the other, we have analyzed changes in the vibrational spectra of the molecules at specific adsorption sites, as a probe to follow molecular adsorption processes locally. In particular, we find additional peaks in the vibrational spectra of molecules close to kink sites which exhibit a characteristic Fano-like line shape. From our data, we infer the possible existence of selection rules in the excitation or in the detection mechanism, based on symmetry.

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